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Destroying Chemical Wastes in Commercial-Scale Incinerators

Arthur D. Little, Inc, Cambridge, Mass

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DESTROYING CHEMICAL WASTES IN COMMERCIAL-SCALE INCINERATORS

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16. Abstracts

Tests were conducted at Zimpro, Inc., Rothschild, Wisconsin, to determine the effectiveness of wet air oxidation for destruction of two selected aqueous industrial wastes: coke plant waste and Amiben® (herbicide) manufacturing waste. A pilot-scale facility was tested for the coke plant waste with <6g/l total solids and 3.3 g/l Biological Oxygen Demand (BOD_5), chemical compounds such as cyanides, phenols and cresols were 99% destroyed; BOD_5 and Chemical Oxygen Demand (COD) were reduced by about 90%. The concentration of quinoline was reduced by only 66%. Estimated costs for treating 2,129 cu m/day of coke waste were: $12.3 MM capital investment and $9.90/cu m total operating cost. For the Amiben® waste, with 55 g/l total solids and 31 g/l BOD_5, the test showed >99% destruction of the major organic waste components, dichloronitrobenzoic acids, with about 10% conversion to an intermediate degradation product, dichloronitrobenzene. The BOD_5 and COD were reduced by 90% and 82%, respectively. Estimated costs for treating 151 cu m/day of Amiben waste were: $2.2 MM capital investment and $18.00/cu m total operating cost.

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FOREWORD

The tests described in this report are part of a program designed to evaluate the environmental, technical, and economic feasibility of disposing of industrial wastes via incineration. This objective is being pursued through a series of test burns conducted at commercial incinerators and with real-world industrial wastes. Approximately eight incineration facilities and seventeen different industrial wastes will be tested under this program. The incineration facilities were selected to represent the various design categories which appear most promising for industrial waste disposal. The wastes were selected on the basis of their suitability for disposal by incineration and their environmental priority.

This report describes the test conducted at Simpro, Inc., (Rothschild, Wisconsin), which was the fourth facility of the series. Facility reports similar to this one have been published for the first three tests which were conducted at the Marquardt liquid injection facility in Van Nuys, California, the Surface Combustion pyrolysis facility in Toledo, Ohio, and the Systech fluidized bed facility in Franklin, Ohio. The facility reports are primarily of an objective nature presenting the equipment description, waste analysis, operational procedures, sampling techniques, analytical methods, emission data and cost information. Facility reports are published as soon as possible after the testing has been completed at a facility so that the raw data and basic results will be available to the public quickly.

In addition to the facility reports, a final report will also be prepared after all testing has been completed. In contrast to the facility reports which are primarily objective, the final report will provide a detailed subjective analysis on each test and the overall program.

ACKNOWLEDGEMENTS

Arthur D. Little, Inc., is grateful to the Simpro, Inc., personnel for their cooperation in conducting these facility tests. Acknowledgement is also made of the extensive and fruitful interactions between ADL and TRW personnel during the initial phases of this program. The project is deeply indebted to Messrs. Alfred Lindsey and John Schaum, of the Office of Solid Waste Management Programs, U.S. Environmental Protection Agency, for their advice and technical direction.

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1. SUMMARY

In the Environmental Protection Agency's Program to determine the capabilities of thermal methods for the destruction of chemical wastes, wet air oxidation is one of seven different methods being investigated. Wet air oxidation is carried out in an aqueous medium with high pressure air at temperatures typically between 130°C (266°F) and 350°C (662°F). Wet air oxidation tests were carried out on (1) coke plant wastes, and (2) Amiben® wastes in a mobile industrial pilot plant operated by Zimpro, Inc., at its Rothschild, Wisconsin, Facilities.

Both a gaseous and aqueous stream result from wet air oxidation and the products of destruction may be found in either stream. The major portions are expected to remain with the aqueous stream. In addition, an oxidation catalyst such as a copper compound may be required and will remain in the aqueous stream. The pertinent operating conditions, chemical components, destruction efficiencies, and chemical components of major environmental concern in the effluents are summarized in Table 1-1. Inspection of these data indicate that chemical compounds such as cyanides, phenols, and cresols in coke plant wastes are 99% destroyed, while the Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) are reduced by about 90%. Also, the relative resistance of some chemical species to wet air oxidation is indicated by only a 66% reduction in quinoline concentration. The possibility of producing an intermediate degradation product is demonstrated clearly in the case of Amiben® wastes where the dichloronitrobenzoic acid isomers are degraded to dichloronitrobenzene. Consideration of the composition of the aqueous and gaseous effluent streams indicates that further treatment of the aqueous stream would undoubtedly be required before discharge, a requirement usually expected with wet air oxidation. However, discharge of the gaseous streams without further treatment could be expected.

Consideration of the process and economic aspects of wet air oxidation indicated its major applications will be to aqueous waste streams containing organic chemicals with concentrations either too high or too toxic for biological systems and with energy content too low for economic destruction by high temperature incineration. Estimated capital investments and annual operating costs for coke plant and Amiben® wastes are as follows:

® Trademark of Rorer-Amchem, Inc., Philadelphia, Pa.

	COKE PLANT		AMIDE/MP WASTE	
Capacity	7,140 cu m/day (360,000 gal/day)		151 cu m/day (40,000 gal/day)	
Estimated Capital Investment	$12.3 MM		$2.2 MM	
	$/year	$/cu m	$/year	$/cu m
Direct Operating Costs	$3.6 MM	$5.15	$0.3 MM	$ 6
Indirect Operating Costs	$3.3 MM	$4.75	$0.6 MM	$12
Total Estimated Operating Costs	$6.9 MM	$9.90	$0.9 MM	$18

The results of this work show that wet air oxidation is a feasible method for achieving a high degree of destruction of a variety of organic chemicals contained in aqueous streams and should be considered, therefore, as a prominent technology for destruction of certain chemical wastes.

TABLE 1-1

SUMMARY OF EFFECTIVENESS OF WET AIR OXIDATION FOR TREATMENT OF COKE PLANT WASTE AND ARMSCO* WASTE

COKE PLANT WASTE

Operating Conditions 279°C (535°F)
107 Atmospheres of Pressure
1.15 Hour Residence Time

Concentration mg/liter

Waste Component	Feed	Effluent	% Destruction
Cyanide	309	<3	>99
Phenol	743	1.05	99.9
Cresol	188	< .2	99.9
Quinoline	38	13	65.7
BOD_5	2083	23	98.9
COD	5520	481	91.3

Components of Major Environmental Concern in Effluents:

Aqueous Stream: Quinoline at 13 ppm
(Copper at 750 ppm)*
NH_3, 2410 mg/l as N

Gaseous Stream: 180 ppm Hydrocarbons
1050 ppm Carbon Monoxide

ARMSCO* WASTE

Operating Conditions 282°C (540°F)
107 Atmospheres of Pressure
1 Hour Residence Time

Concentration, g/liter

Waste Component	Feed	Effluent	% Destruction
2,5 Dichloro-4-Nitrobenzoic acid plus 2,5 - Dichloro -3- Nitrobenzoic Acid	19.1	<0.1	>99
BOD_5	5.28	0.50	90
COD	30.5	2.92	62

Components of Major Environmental Concern in Effluents:

Aqueous Stream: 2,5 Dichloronitrobenzene, at 2.0 g/l
(Copper at 386 ppm)*

Gaseous Stream: 750 ppm Hydrocarbons
3210 ppm Carbon Monoxide

*The copper is added to the waste as an oxidation catalyst and is normally recovered from the process effluent.

2. INTRODUCTION

The U. S. Environmental Protection Agency has sponsored a program[a] to evaluate the effectiveness of a variety of types of commercial thermal destruction facilities for destroying chemical wastes. Wet air oxidation was selected as one method for testing because it offers the potential for thermal treatment of wastes with low heating values, such as aqueous streams containing low concentrations of organic materials.

The objective of this program was to evaluate the capabilities of commercial scale facilities. However, a full scale wet air oxidation facility could not be located within the continental United States which would be available for this test program. It was decided to conduct a series of tests using the pilot plant unit operated by Zimpro, Inc., in Rothschild, Wisconsin. The unit tested is used on a regular basis by Zimpro, Inc., in determining the design conditions for its wet air oxidation systems. The facility is described in detail in Section 3 of this report.

The two chemical wastes selected for testing at this wet air oxidation facility were those which, based on the information supplied by the waste generators, would be difficult to treat in other types of thermal destruction facilities. The criteria for selection included:

- the waste should be an aqueous solution containing oxidizable pollutants
- the total heating value could be low (<3000 Btu/lb)
- substantial quantities of sulfates and chlorides could be tolerated and there were no intrinsic restrictions on elemental composition
- the waste should represent a high priority disposal problem in terms of potential hazard and/or annual volume generated.

The wastes selected for testing, and the descriptions of these wastes originally provided by the waste generators, were:

- Coke plant wastes. Weak ammonia liquor containing phenols, cyanides, chlorides, sulfates and total dissolved solid content of approximately 6000 mg/l.

[a] Contract No. 68-01-2966

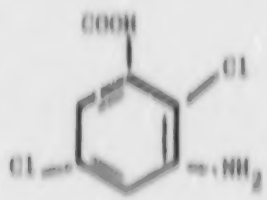
- Amiben® manufacturing wastes.* Liquid containing 90% water, 5% isomers of Amiben, and 5% sodium chloride and sodium sulfate.

The materials actually received for testing were generally in accordance with these descriptions, except that the Amiben® waste contained by-products of Amiben® manufacture rather than isomers of Amiben®.

Each waste was tested at a single set of operating conditions in the equipment described in Section 3. The test conditions chosen were based on the results of laboratory autoclave runs prior to the test. The test procedures are described in Section 4 of this report.

Detailed information on process and analytical data are in Appendices A, B and C. The test results are summarized and discussed in Section 5 of the report. Also in the report are estimates of capital and operating costs for treatment of the two wastes by full-scale wet air oxidation facilities (Section 6). Overall Conclusions are presented in Section 7.

* Amiben® is an herbicide with the molecular structure:



3. PROCESS DESCRIPTION

The wet air oxidation facility used in this program is a mobile industrial pilot plant owned by Zimpro, Inc. It is a completely self-contained system housed in a 40-foot semi-trailer. The titanium reaction vessels can be operated within the following limits:

Maximum pressure	210 atm (3600 psig)
Temperature range	230 - 325°C
Reactor residence time	0.6 hr minimum
Maximum flow rate	40 liters/hr

The process conditions chosen for these tests were a pressure of 107 atm, a temperature of 280°C with a liquid residence time of one hour.

3.1 TEST FACILITY

The Zimpro wet oxidation system as used for this test program is shown schematically in Figures 3-1 and 3-2. The 25 liters of reactor volume is divided equally between two vessels so that it can fit into the trailer. The vessels are constructed of titanium so that they can handle a wide variety of chemical conditions.

The test system included the following components:

- feed tanks
- centrifugal type feed pump
- high pressure waste pump
- high pressure catalyst injection system
- high pressure air supply
- feed preheater
- two reactors (in series)
- effluent cooler
- pressure reducing valve
- gas-liquid separator
- vent-gas scrubber
- oxidized liquor storage tanks

In the Amiben® waste test, an additional process operation, solvent extraction, was required. The process components are shown in Figures 3-3 through 3-10. Instrumentation included monitoring and control of temperature in the reactors, control of pressure, monitoring of percent residual oxygen in the vent gases and measuring the flow rate of the vent gases. All components of the pilot plant which come in contact with the wastes at high temperature are made of titanium.

In operation, the aqueous waste stream containing oxidizable components is pumped from the feed storage tanks using a centrifugal pump to feed the high pressure positive displacement type pump. There is a recycle line to the feed tank to handle the excess flow and to provide mixing of the feed.

FIGURE 3-1 PLAN DESCRIPTION OF MINERAL INDUSTRIAL PILOT PLANT

Source: Zimpro, Inc.

FIGURE 3-2 FLOW DIAGRAM OF WASTE INDUSTRIAL WATER PLANT
WET OXIDATION OF AMMONIA BASE

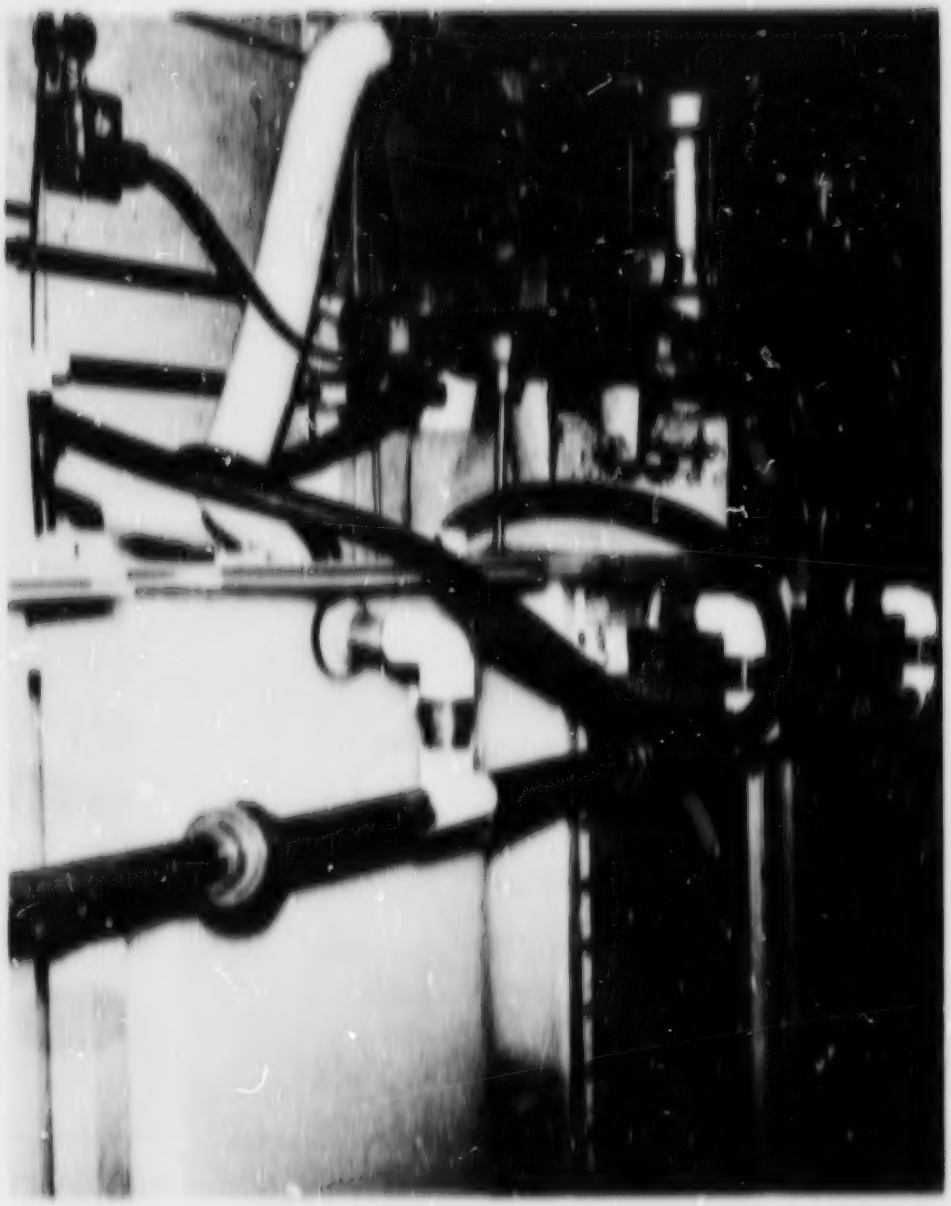


FIGURE 3-3: FEED STORAGE AND MIXING TANKS

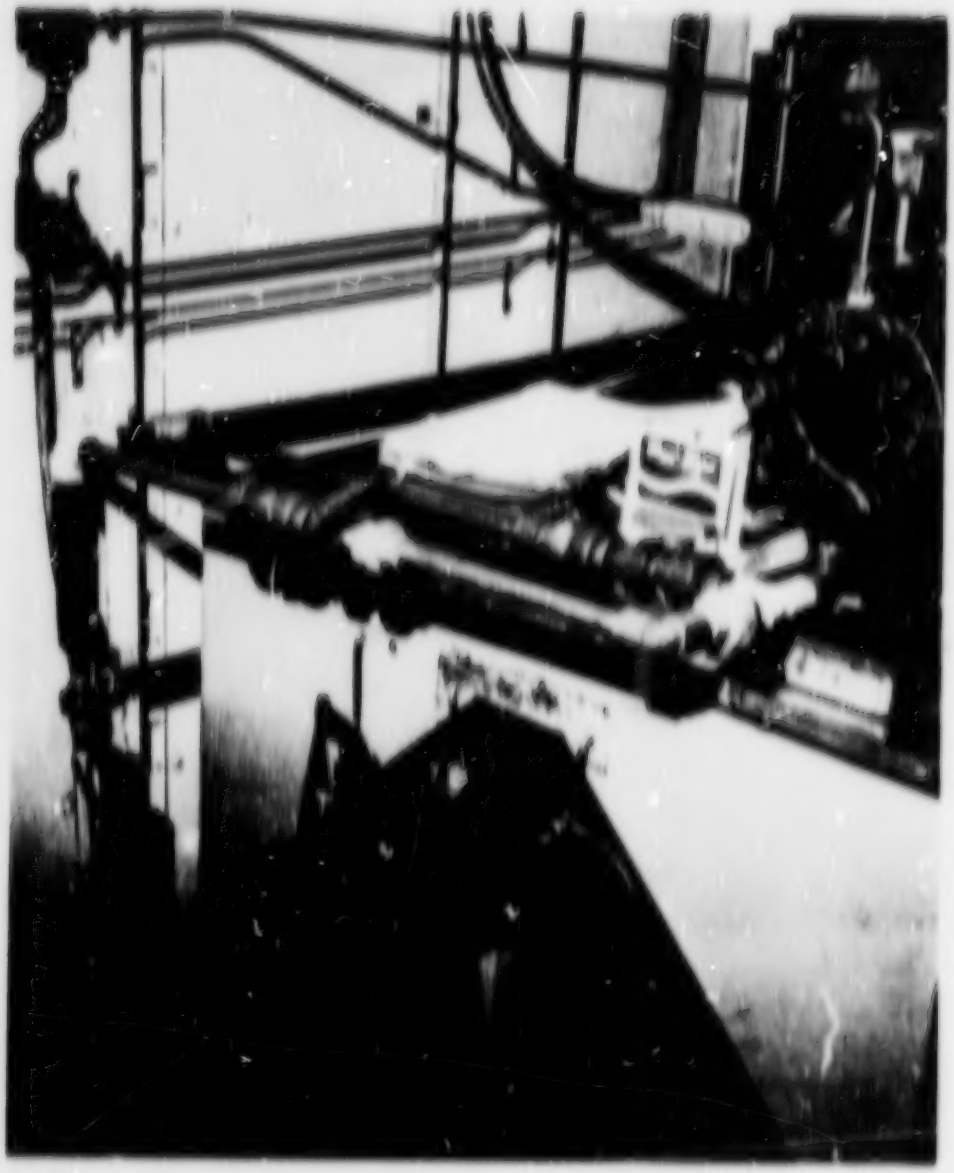


FIGURE 3-41 HIGH PRESSURE FEED PUMP AND RECYCLE PIPING

FIGURE 1-5: REACTOR SYSTEM (left to right: feed preheater, REACTOR NO. 1, REACTOR NO. 2, cooler)

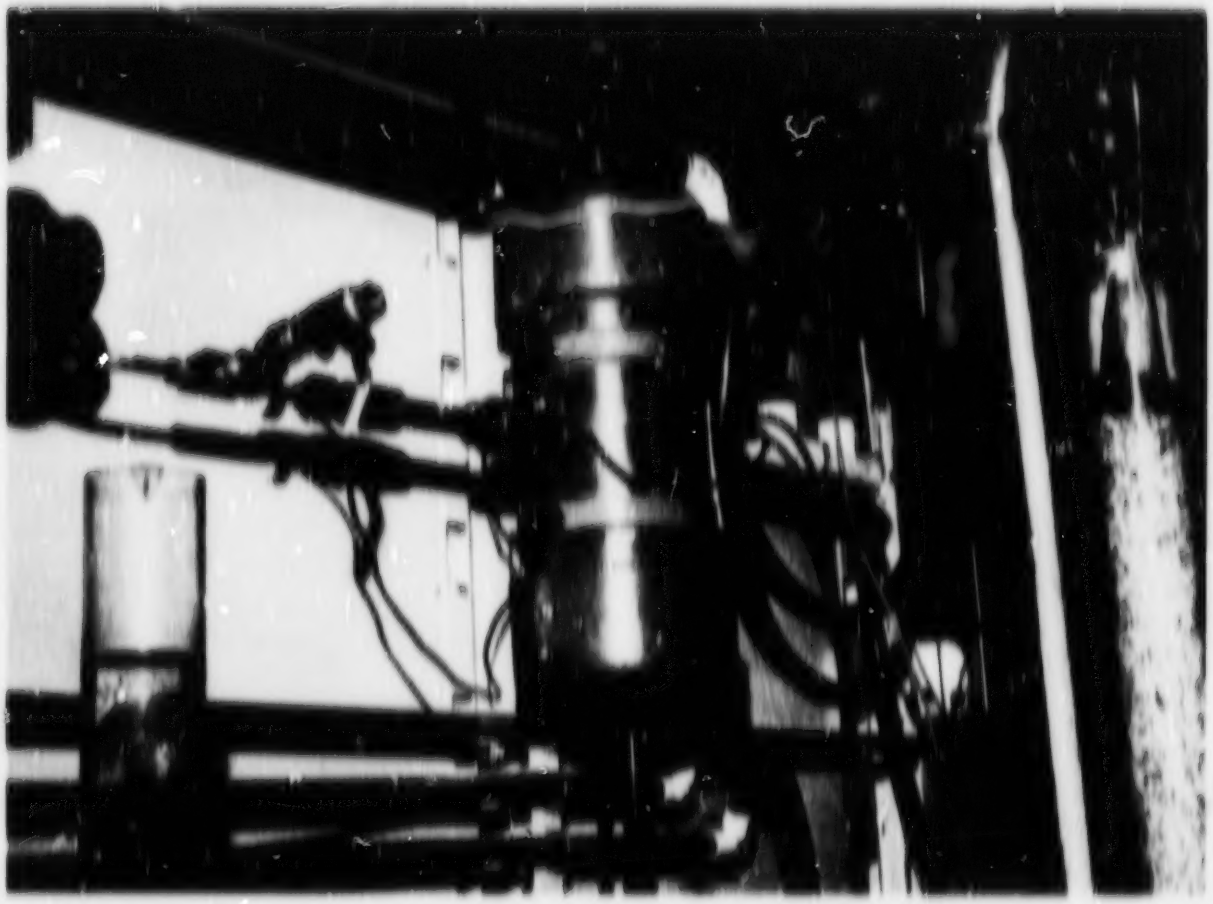


FIGURE 3-6: GAS-LIQUID SEPARATOR

FIGURE 3-7: OXIDIZED LIQUOR TANK (white container on floor)

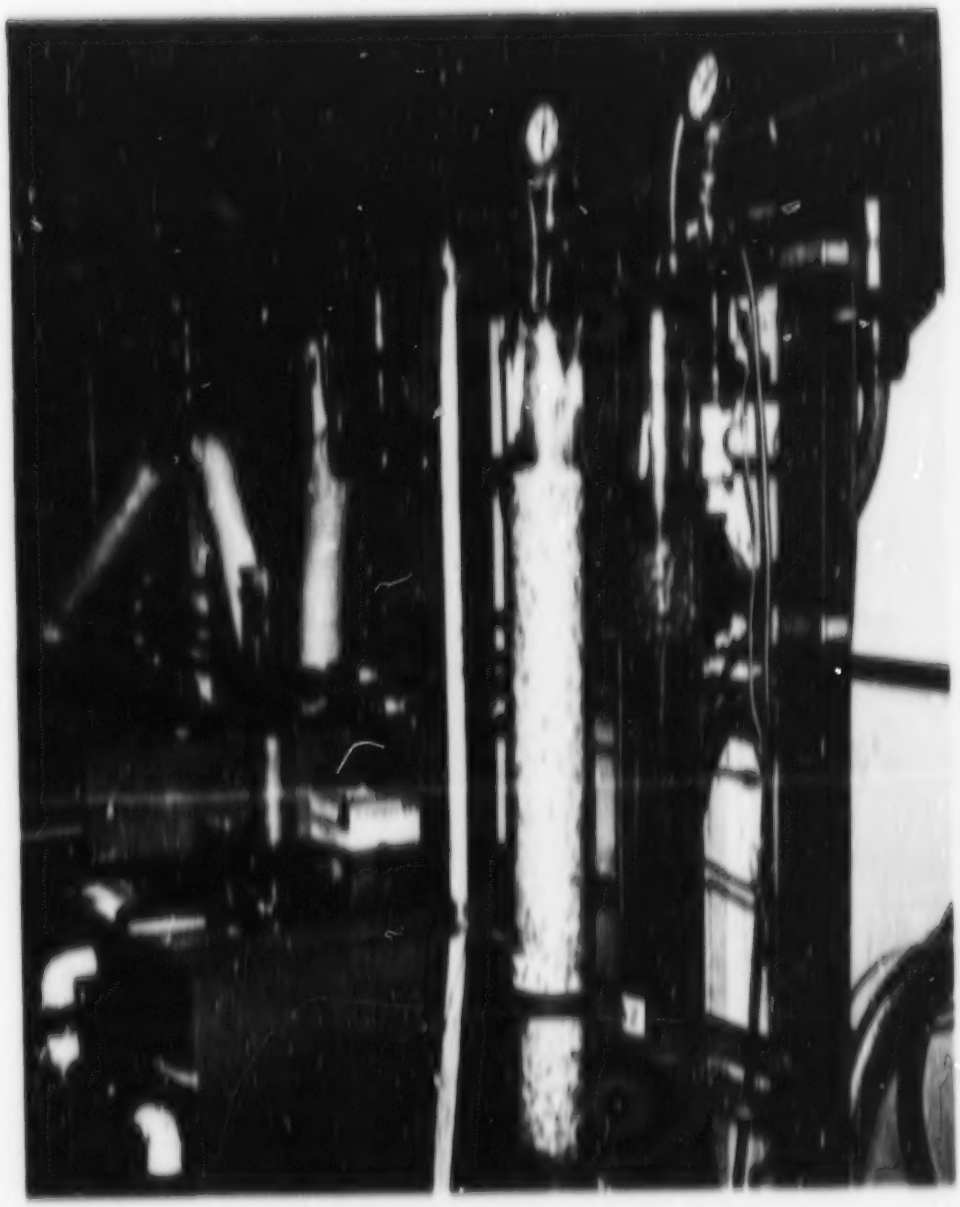


FIGURE 3-81 OFF-GAS SCRUBBERS

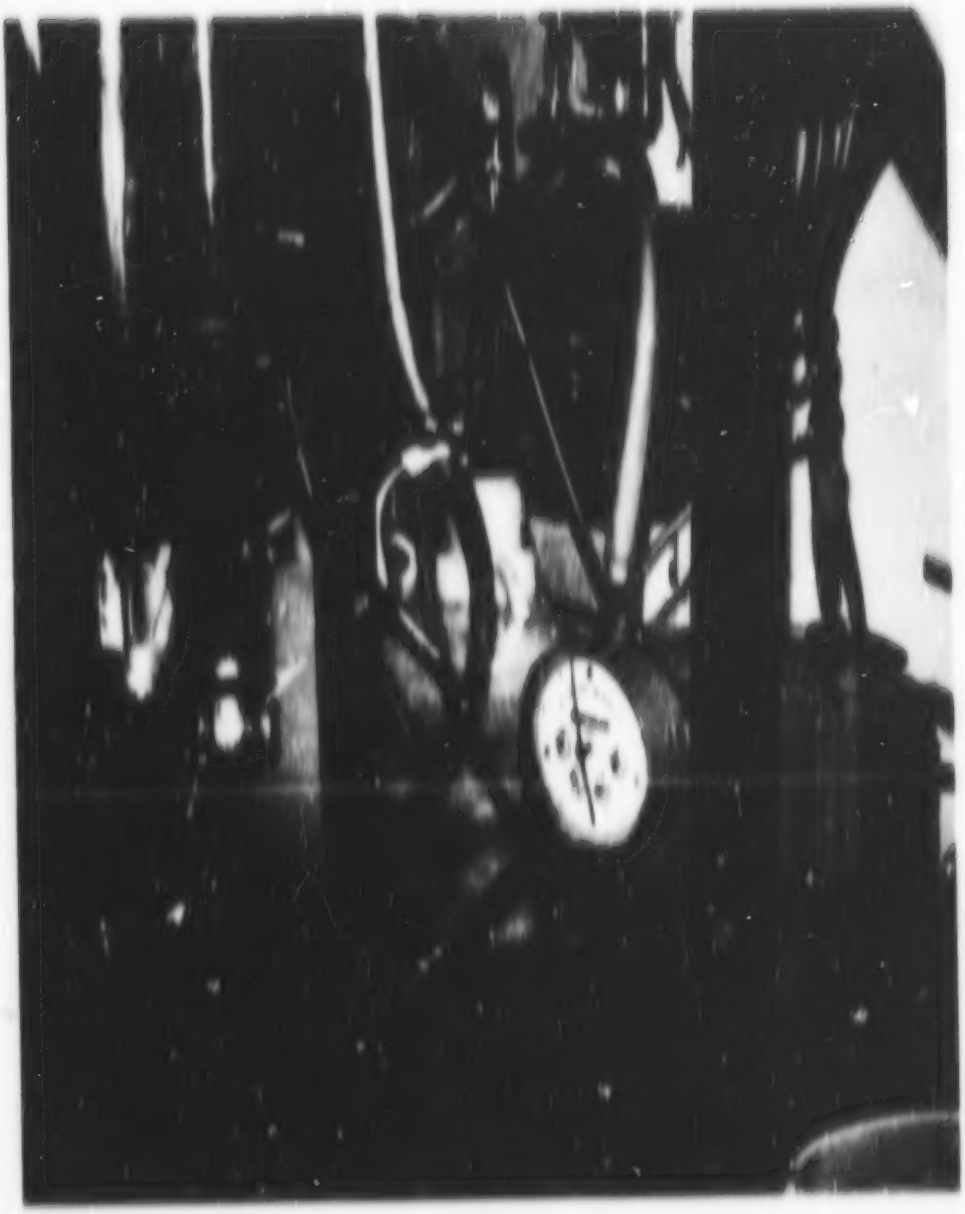


FIGURE 3-9: OFF-GAS METER

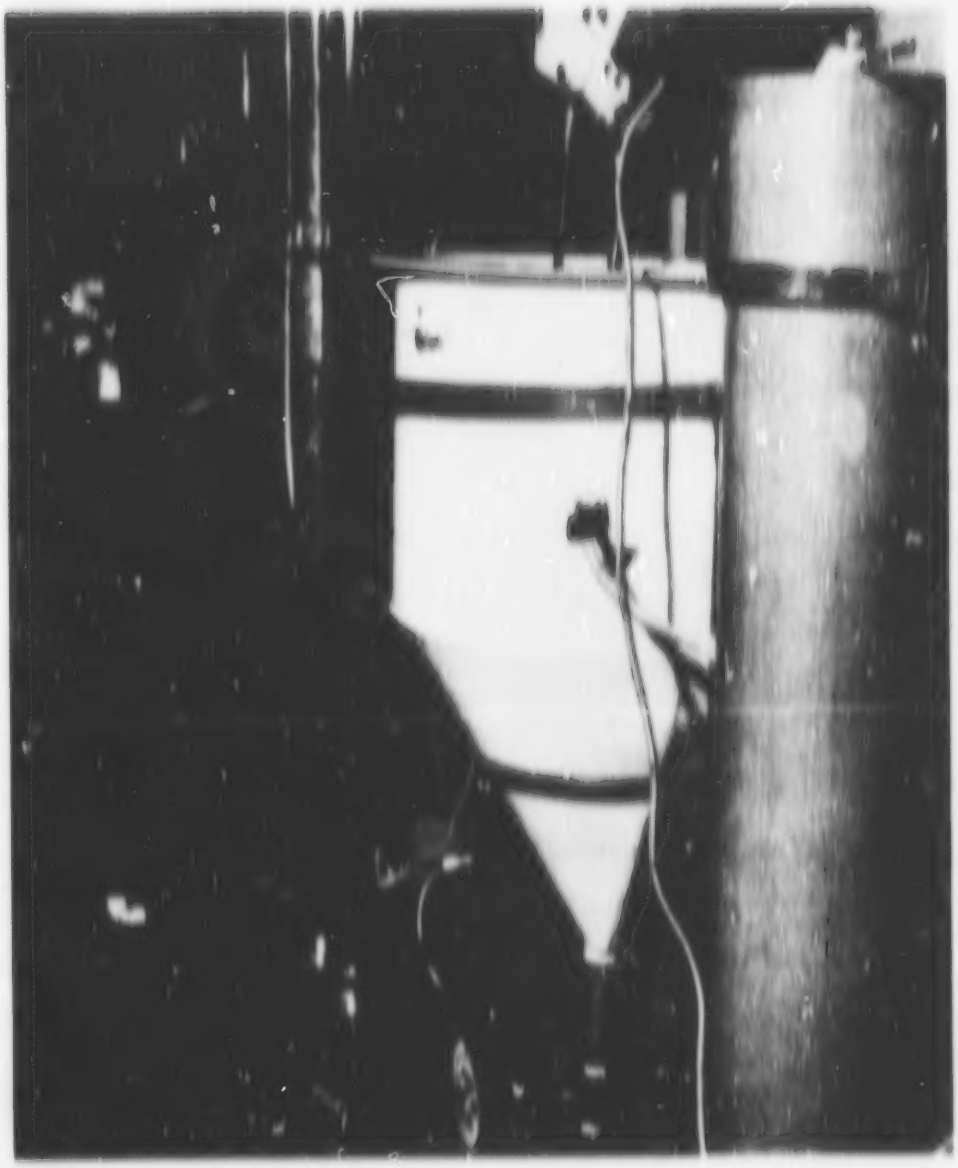


FIGURE 3-10: EXTRACTION VESSEL

The waste then flows through the hot oil preheater into the wet oxidation reactors. In full-scale operation it would acquire heat from the hot oxidised effluent. The temperature of the incoming feed is increased to a level which will support the oxidation reaction in the reaction vessel. In the pilot plant the temperature of the feed to the reactor was maintained approximately 10°C higher than the desired reactor temperature. This was necessary to compensate for the direct injection of cold catalyst solution into the first reactor and the high heat loss from the small components of the pilot plant. The heat generated during wet oxidation was rather low because of the low chemical oxygen demand of the wastes.

Most of the air required for oxidation is mixed with the waste prior to entering the hot oil preheater in the pilot plant. This is done to prevent possible polymerization of the feed and plugging of the preheater which may occur at high temperature. The preheater in the pilot test facility is a spiral wound coil of titanium tubing immersed in a hot oil bath. The air flow resulting from the lowest setting of the valves exceeded the quantity required for oxidation.

Catalyst solution was directly injected into the bottom of the first reactor. It has been observed that addition of catalyst to the feed at ambient temperatures results in precipitation of solids which may plug the preheater coil. A small volume of air is added along with the catalyst solution to keep the catalyst injection line from plugging.

The reactors in the wet air oxidation process are non-mechanically agitated vertical trayed pressure vessels. The normal operating temperatures range from 150 to 320°C at corresponding pressures of 15 to 205 atm. Wet oxidation is based upon the phenomenon that oxidisable materials carried in water will undergo oxidation when the wastewater is heated under pressure and in the presence of air. The oxidation reaction begins to take place at the bottom of the first reactor where all of the streams, waste, and catalyst air are mixed. As oxidation progresses through the reactor, heat is liberated, increasing the temperature of the reaction mixture. The hot oxidised effluent, comprised mainly of steam, water, carbon dioxide and nitrogen, is cooled in a heat exchanger.

Following cooling the pressure is reduced through a control valve and the liquid and gas phases are separated. The oxidised waste then flows to product storage tanks while the gas stream is monitored by a continuous oxygen analyser. The off-gas is sent to the scrubber and is then metered before venting to the atmosphere.

The oxidation of the wastes was carried out using a copper base catalyst. The catalyst was removed from the oxidised liquor by sulfide precipitation. The vent gases were scrubbed by contacting with ordinary tap water at ambient conditions. Scrubbing was accomplished in a 10.2 cm (4 inch) diameter, 1.83 meter (6 ft) high cylindrical tower packed with 1.25 cm (1/2 inch) ceramic saddles with gas and liquid flowing countercurrently.

A nominal water flow rate of 15.1 liter/hr (4 gal/hr) was maintained against an average gas flow rate of approximately 2.55 cubic meters/hr (90 cfh).

The gas sampling and analysis train was connected to the vent gas outlet line downstream from the scrubber and meter. Samples of the oxidized waste were obtained from the oxidized product storage tanks after catalyst removal. In the Amiben® waste test, samples were taken of the oxidized waste stream after solvent extraction and catalyst removal.

Liquid effluents from the tests were to be sent either to a disposal lagoon for which monitoring wells exist, or to a sewage plant operated by Zimpro, Inc. Laboratory tests were used to determine when the treated effluents could be safely introduced into the sewage plant.

Contaminants in the waste tend to stay in the aqueous phase in the wet air oxidation process. They end up in their highest oxidation states in the effluent. Such materials as sulfur compounds, chlorinated hydrocarbons or heavy metals therefore end up as sulfates, chlorides, or heavy metal salts. The effluent gas that is discharged contains mostly spent air and carbon dioxide. As our on-line instruments indicated, however, there are concentrations in the ppm range of carbon monoxide, hydrocarbons, and nitrogen oxides. These contaminants could require emission control if present in high enough concentrations. Simple scrubbing will most probably be sufficient to minimize these contaminants in the gas effluent.

3.2 PROCESS PARAMETERS

Zimpro, Inc., was authorized to perform batch laboratory oxidation tests to determine the optimum reaction conditions for the pilot scale wet air oxidation of the coke plant and Amiben® wastes. These tests were performed in shaking autoclaves. The dependence of oxidation on temperature, reaction time and catalyst addition was determined and the reaction conditions for the pilot runs were set on this basis. Oxidation conditions at 280°C (536°F) and one hour reaction time with catalyst present appeared optimum to achieve more than 90% reduction in COD for both wastes. Under these conditions, laboratory oxidations of coke waste indicated that the destruction of cyanides and phenols was in excess of 99.5%.

Table 3-1 summarizes the actual pilot scale test conditions for the two runs (Amiben® waste and coke plant waste) as well as the test conditions which were determined in laboratory tests by Zimpro, Inc., prior to the pilot waste tests monitored by the ADL staff.

The unusually high excess oxygen concentration in the gaseous effluent from oxidation of waste is a result of the low COD of the waste. The twelve percent excess oxygen concentration would have given a vent gas

TABLE 3-1

SUMMARY OF WET OXIDATION TEST CONDITIONS[A]
PLANNED[AA] AND ACTUAL

	Coke Plant Waste		Amiben® waste	
	Planned	Actual	Planned	Actual
Waste Feed Rate, liter/hr	23.8	20.8	23.8	24.2
gal/hr	6.3	5.5	6.3	6.4
Reactor Residence Time	1 hr	≈1 hr	1 hr	≈1 hr
Reactor Temperature, °C	280	279	280	281
Reactor Pressure, atm	107	107	107	107
Catalyst Addition	Yes	0.3 gph	Yes	0.3 gph
Effluent Gas Vent Rate, cu m/hr	0.8	2.5	-	2.9
cfm	0.5	1.5	-	1.7
Excess O_2 in Vent Gas, %	12	16.3	3	8.8

[A] operating data collected by Zimpro, Inc. personnel

[AA] determined by Zimpro, Inc. in laboratory scale autoclave tests.

flow rate of approximately 0.8 cubic meters/hr. In the actual test, closer to 16 and 17 percent was observed which gave a flow rate of approximately 2.5 cubic meters/hr. This was caused by the inability to control the high pressure air addition at a lower flow rate. Wastes with this low COD value are not normally encountered in wet air oxidation. Actually, for the coke plant waste test, the greater flow rate of vent gas provided an extra measure of safety for the on-line instruments and the sampling train since, as planned prior to the actual test, the instruments would have been drawing a large quantity of the total stream volume. The effluent gas flows were monitored using a standard gas meter. Due to the limited accuracy of the inlet high pressure air measurements normally made for the system (the air flow was very low because of the low COD of the waste) the amounts of air fed to the wet-air oxidation system were calculated using the inlet and outlet COD's and the excess oxygen in the effluent gas stream. Temperatures and pressures were measured by instrumentation already in place in the pilot facility. The location of these measuring points is indicated in Figures 3-1 and 3-2. The temperatures were measured with thermocouples and recorded by a strip chart recorder. Waste feed rates were measured by monitoring the feed tank level for the wastes. The system operating parameters were recorded hourly by Zimpro operating personnel according to previously specified and agreed upon procedures. After a period of operation with relatively constant readings by the on-line gas stream monitoring instrumentation in the trailer, a three hour complete sampling was performed by the ADL staff of the feed, effluent and gas streams.

4. TEST DESCRIPTION

4.1 WASTES TESTED

The two wastes tested at Zimpro, Inc., were coke plant waste and wastes from production of Amiben.® Survey samples were received well in advance of the tests and analyzed in order to determine appropriate sampling procedures. The results of those survey analyses are summarized below.

4.1.1 Coke Plant Waste

The coke plant waste was a clear, light brown, aqueous solution with a few flecks of black particulate material. It had a pH of about 9 and a residue on ignition of 0.3%. The total dissolved solids content was 1%, of which 5-10% was organic material. Elemental analysis of a sample evaporated to dryness showed the following composition: C, 6.01%; H, 7.05%; N, 24.82%; S, 5.50%; $CO^{=}$, 48.63%.

Organic species detected in the waste and their relative abundances were: phenol, 1.0; cresols, 0.65; indole, 0.20; quinoline, 0.18; aniline, 0.02; napthalene, 0.01; dimethylphenols, 0.01; and diphenyl sulfide, trace. Major inorganic components were NH_4^+, Cl^-, $SO_4^=$ and CN^-. Examination of the waste by x-ray fluorescence showed chlorine, sulfur, calcium, bromine, potassium, zinc and phosphorus.

The higher heating value of the waste was estimated at <55 Kcal/Kg (100 Btu/lb).

4.1.2 Amiben® Waste

Two Amiben® wastes were available, taken before and after "well" pre-treatment. The two wastes were essentially the same except for pH and it is understood that the well treatment is simply a neutralization and some filtration. The "before", or basic, Amiben® waste was chosen because the wet oxidation process will produce some acids and thus partially neutralize the basic waste. All data in this report pertain to the basic, before treatment, Amiben® waste.

The waste was a clear, amber aqueous solution with a pH of approximately 9. The total solids content was 6-7% and the ash content was 3.6%. The organic content was therefore about 3-3.5%. Elemental analysis of a sample evaporated to dryness showed the following composition: C, 22.79%; H, 0.78%; N, 3.47%; S, 11.55%; and Cl, 24.96%.

Organic species detected in the waste and their relative abundances were: dichloronitrobenzoic acid isomer, 1.0; a second dichloronitrobenzoic acid isomer, 0.15; trichloronitrobenzoic acid, 0.14; and, substituted biphenyls, 0.02. The major inorganic species appeared to be sodium sulfate and sodium chloride. Examination of the waste by x-ray fluorescence showed chlorine, sulfur, potassium, calcium, iron and copper.

The higher heating value of the waste was estimated at <55 Kcal/Kg (100 Btu/lb).

4.2 OPERATIONAL PROCEDURES

Detailed test procedures, including a test plan and safety plan were reviewed prior to arrival of the ADL sampling team onsite. The test procedure was as follows:

Test Procedure

- Feed tanks were filled with the waste to be treated. Continuous stirring was maintained in the tanks to avoid settling of solids.
- The hot oil preheater was turned on while circulating water through the unit and the system pressurized to 107 atm (1560 psig).
- When reactor inlet temperature reached approximately 260°C (500°F) the feed to the system was switched from water to waste and the flow of high pressure air was started. The air flow rate was maintained at the lowest possible valve opening.
- Injection of catalyst solution (directly into the first reactor) was started along with minimal addition of air to the catalyst injection line.
- When the reactor temperature reached 280°C (536°F) hourly log book entries and sample collection were started by Zimpro personnel.
- After two to three hours of steady reactor temperature oxidized effluent collection was started.
- As required, feed tanks were filled with the waste. Feed samples were drawn on several occasions during the run and analyzed by Zimpro, Inc. to determine any differences in feed composition.

- When relatively constant gas effluent analyses were reflected by the on-line monitoring instruments in the test trailer, steady state operation was assumed and the ADL staff collected appropriate feed, oxidized liquid effluent and effluent gas samples for a three-hour period. Since Zimpro personnel normally perform 24 hour tests, the test run would then continue until Zimpro testing was complete.

- The copper catalyst was removed from the oxidized waste by sulfide precipitation.

- During shutdown the hot oil preheater was turned off and feed to the unit was switched back to water. After the several hour period required to cool the system the flow of water and air was stopped and the system depressurized.

The following additional procedure was used with the oxidized Amiben® waste:

- The composite effluent was stirred vigorously in the storage tanks and then transferred to the extraction vessel.

- Perchloroethylene was added to the effluent maintaining a volume ratio of 10:1 of effluent to solvent.

- The mixture was stirred for a few minutes and the phases allowed to separate.

- The perchloroethylene layer and the interface layer were removed separately from the bottom of the extraction vessel. A sample of the raffinate was then drawn.

- The remaining raffinate was then contacted with fresh perchloroethylene and the above procedure repeated. A total of three extractions were performed.

4.3 SAMPLING METHODS

Samples were collected over a three-hour period during steady-state operation for each waste. The types of samples taken were:

- Bulk samples of aqueous waste feed, aqueous reactor effluent, scrubber water feed and spent scrubber water.
- Sample of vent gas fed to on-line instruments for continuous monitoring of test.
- Grab samples of vent gases.

In addition, Zimpro, Inc., supplied samples of process effluents which had been treated in batch processes after the wet air oxidation.

4.3.1 Bulk Liquid Samples

One-liter samples of liquid streams were taken in Nalgene bottles at hourly intervals over the course of the 3-hour sampling period. The four samples of each stream were composited in the laboratory.

4.3.2 On-Line Monitoring

The entire flow of vent gas from each waste test was conducted via 37 mm polyethylene tubing into the EPA trailer, (Figure 4-1). A portion of this vent gas was tapped off and passed to a gas conditioning system. The gas conditioner was designed to deliver a cool, dry, particulate-free sample to the CO, CO_2, O_2, and NO analysers. A fraction of the sample was also supplied, untreated, to the hydrocarbon analyser.

The instruments used and their ranges were:

Hydrocarbons	Beckman Model 402	0.05 ppm- 10%
Carbon Monoxide	Beckman Model 865	2-220 ppm
Carbon Dioxide	Beckman Model 864	0.05 - 20%
Oxygen	Taylor OA 271	0.05 - 100%
Nitrogen Oxides	Thermo Electron Model 10A	0.05 ppm- 1%

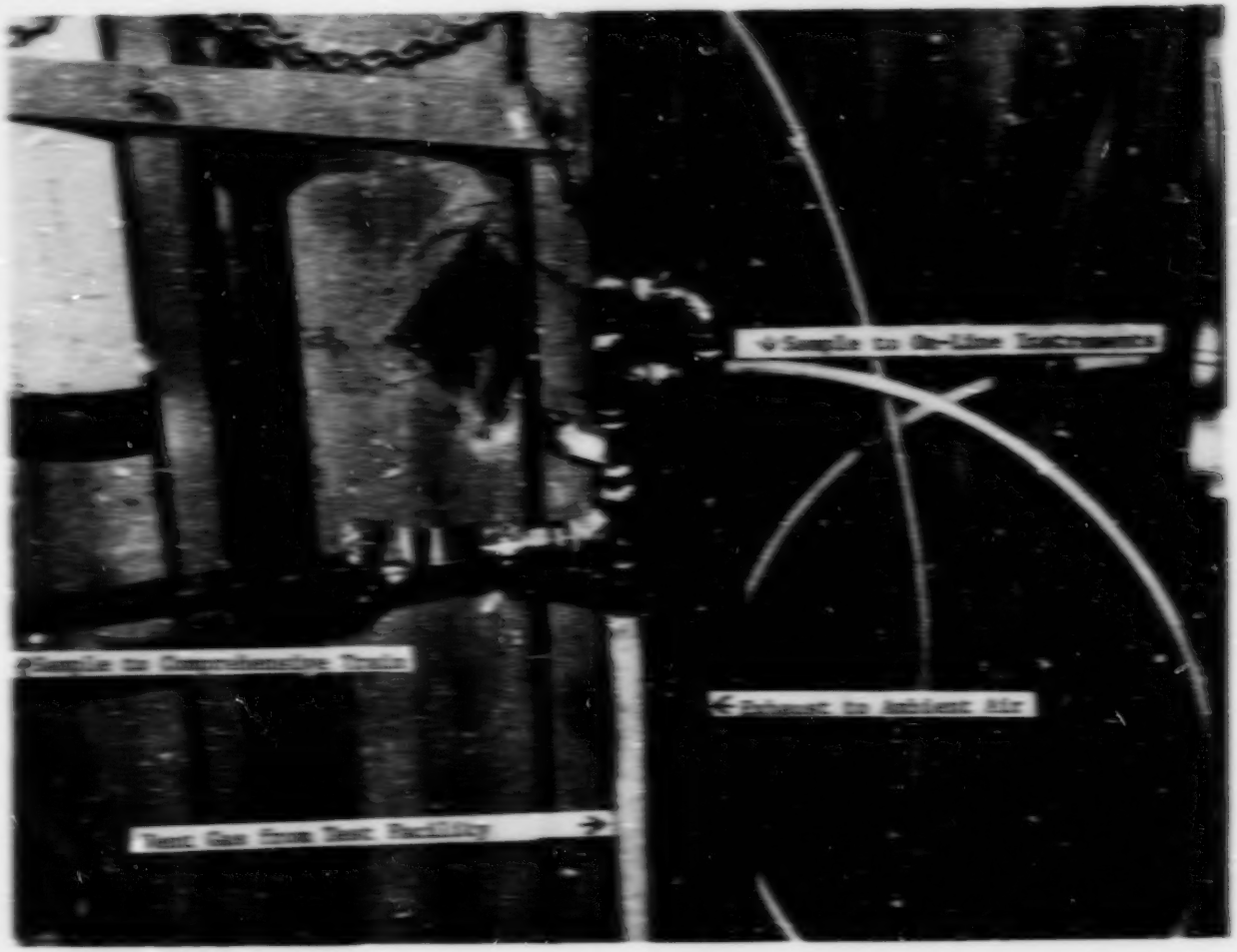


FIGURE A-1: PHOTOGRAPH OF VENT GAS SAMPLING INTERFACE

4.3.3 Comprehensive Sampling Train

The train used for collecting a sample of vent gas is shown schematically in Figure 4-2 and in the photograph in Figure 4-3. The principal components in this comprehensive sampling train were:

- a 1.2 cm (0.5") pyrex sampling probe,
- a quartz fiber filter,
- a sorbent trap filled with XAD-2®* resin to collect organics of moderate volatility,
- impingers containing dilute aqueous nitric acid.

A second gas grab sample was collected in a 125 ml glass sampling bulb inserted in the by-pass line from the hydrocarbon analyzer. The bypass line was also sampled using detector tubes for hydrogen cyanide.

An EPA Method 5 sampling procedure involving a multipoint traverse was not appropriate for this facility, since the vent gas pipe had a diameter of only 37 mm (1.5 in) and carried a total flow of <3 cubic meters/hr (<2 cfm).

4.4 ANALYSIS TECHNIQUES

4.4.1 Extractions and Sample Preparation

A detailed description of the specific solvents, etc., used for the Zimpro Samples is given in Appendix A.

4.4.2 Analytical Methods

The techniques which were chosen during Phase I of this contract for evaluation of the effectiveness of thermal destruction of industrial wastes were:

Low Resolution Mass Spectrometry (LRMS)
Infrared Spectrometry (IR)
Gas Chromatography/Mass Spectrometry (GC/MS)
Elemental Analysis

Inorganic analysis methods selected were:

X-ray Fluorescence (XRF)
Spark Source Mass Spectrometry (SSMS)
Atomic Absorption Spectroscopy (AAS)
Specific Ion Electrode Methods (SIE)

* Trademark of Rohm and Haas Company

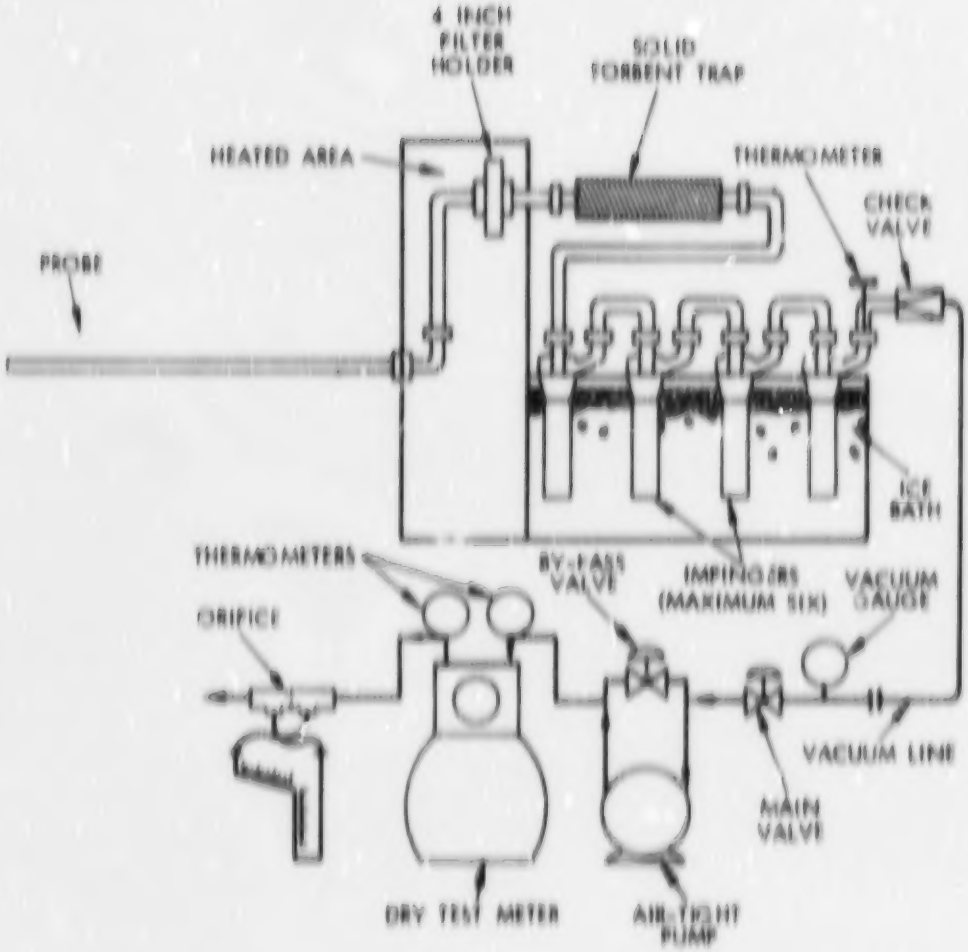


FIGURE A-2: SCHEMATIC OF COMPREHENSIVE SAMPLING TRAIN

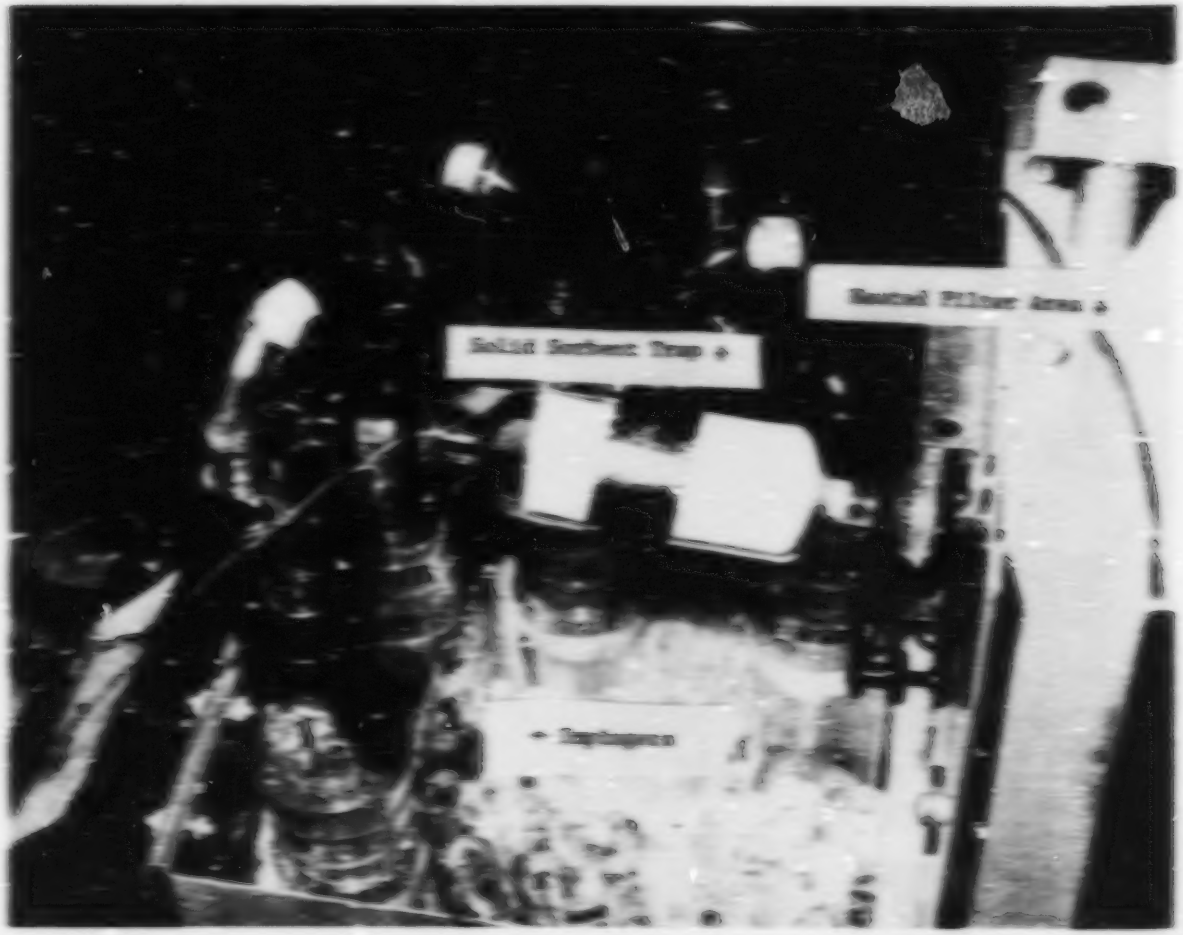


FIGURE 4-1: PHOTOGRAPH OF CONDENSATE SAMPLING TRAIN

These techniques were applied to the Zimpro samples where appropriate. In addition, High Performance Liquid Chromatography (HPLC) was used for quantitative analysis of components of the Amiben® waste. Details of this procedure are given in Appendix A.

4.5 PROBLEMS ENCOUNTERED

In maintaining air flow to the wet oxidation reactors even the lowest possible setting of the valves allowed an amount of air to pass through which exceeded the actual quantity required by oxidation. This resulted in high concentrations of residual oxygen in the vent gases. Also, because of the small size of piping in the oxidation system, there were shutdowns caused by temporary plugging which would not have taken place in larger scale equipment.

Usually the effluent cooler is operated so that the oxidized waste-vent gases mixture from the reactors is cooled to ambient temperature. During oxidation of Amiben® wastes it was observed that decarboxylation of organics takes place in the reactors. This did not take place during laboratory autoclave studies. It is believed that the waste components varied from those used in laboratory tests. The decarboxylated products, which contained principally p-dichoronitrobenzene (p-DCNB), solidified at ambient temperature causing plugging in lines downstream of the cooler, particularly in the control valve. To avoid this plugging, the effluent temperature from the cooler was maintained at about 57°C (135°F) during Amiben® oxidation. Also, in order to obtain a more highly treated effluent from oxidation of Amiben® waste, the decarboxylated organics were removed by multistage batch extractions with perchloroethylene (PERC) at ambient conditions.

5. TEST RESULTS

The results of analyses of feed and effluent samples collected during tests of wet air oxidation of Amiben® and coke plant wastes are summarised and discussed in this Section. A more detailed presentation of the analytical results will be found in Appendix B.

5.1 RESULTS OF COKE PLANT WASTE TEST

5.1.1 Operating Conditions for Coke Plant Waste Test

Operating conditions for the coke plant waste tests are summarised in Table 5-1. More detail is given in Appendix C.

5.1.2 Fate of Organic Components of the Waste

In contrast to the Amiben® waste, the coke plant waste contained a considerable variety of organic species. As Table 5-2 indicates, the major components identified in the coke plant waste were phenol at about 750 mg/l and cresol at about 200 mg/l. Both of these species are recognised as toxic; the reported[4] LD50's are 414 mg/kg and 121 mg/kg (oral, rat), respectively. Also identified in the coke plant waste sample were smaller quantities of aromatic nitrogen-containing compounds, with quinoline, indole and aniline present at > 37 mg/l.

As the data in Table 5-2 indicate, the efficiency of wet air oxidation for destruction of most of the organic components of the coke plant waste is fairly high. The calculated percentage reductions in concentration are: 99.9% for phenol; 99.9% for cresol; and 98.9% for BOD_5. However, the data also indicate that some species are more resistant to oxidation than the phenols. The concentration of quinoline in the effluent is about one-third of that in the waste; corresponding to a destruction efficiency of only 66%. Further evidence for the resistance of some species to oxidation is the fact that COD is reduced by only 91.3%.

No organic products of partial oxidation of phenol or cresol were found in the wet air oxidation process effluents. As the data in Table 5-1 show, the quantity of volatile hydrocarbon stripped from the oxidised waste by the vent gas was small. This quantity of material corresponds to <2% of the carbon in the phenol and cresol originally present in the waste. It is possible that small quantities of highly oxidised, water-soluble species such as acetic acid were present in the effluent, but these could not have been major oxidation products. The available evidence suggests that the major product of wet air oxidation of phenol and cresol was carbon dioxide. The amount of CO_2 found in the vent gas (Table 5-3) is more than enough to account for the organic carbon in the waste.

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[4] "Registry of Toxic Effects of Chemical Substances", 1975 Edition, U.S. Department of Health, Education and Welfare, Rockville, Maryland, 1975.

TABLE 5-1

OPERATING CONDITIONS FOR TESTS ON COKE PLANT WASTES

Waste Feed Rate	20.8 liters/hr (5.5 gph)
High Pressure Air Feed Rate*	2.55 cu m/hr (1.52 cfm)
Catalyst Addition Rate	1.1 liter/hr (0.3 gph)
Reactor Residence Time	1.15 hr
Reactor Temperature	279°C (535°F)
Reactor Pressure	107 atm (1560 psig)
Effluent Gas Vent Rate	9.51 cu m/hr (1.5 cfm)

* ABB Calculated Value

TABLE 5-2

PRINCIPAL COMPONENTS OF FEED AND EFFLUENT AQUEOUS STREAMS FOR COKE WASTE TEST[A]

Component	Concentration, mg/l	
	Feed	Effluent
Organic Species		
Phenol	743*	1.05*
Cresol	188*	< 0.2*
Quinoline	38	13
Indole	41	ND #
Aniline	26	ND
Inorganic Species		
pH	8.8	7.7
Cl^-	3960	3550
$SO_4^=$	2910	2870
CN^-*	309	< 3
NH_3-N*	2410	2380
Collective Parameters		
BOD_5*	3083	33
COD*	5520	481
Total Solids*	5730	8560

* Asterisks indicate data reported by Zimpro, Inc. Others are ADL Values.

N.D. = Not detectable, < 20 mg/l.

TABLE 5-3

CARBON CONTAINING SPECIES IN VENT GAS FROM COKE WASTE TEST

	Concentration in Vent Gas		Equivalent Concentration In Aqueous Waste Stream*	
	ppm	mg/m^3	mg/l	as Carbon mgC/l
Hydrocarbons (as methane)	180	120	15	11
Carbon Monoxide	1050	1200	150	64
Carbon Dioxide	2.30×10^4	42×10^3	5.1×10^3	1.4×10^3

* Equivalence based on approximate total flows of 2.54 m^3/hr of vent gas and 20.8 l/hr of aqueous waste. Therefore, mg/l in waste equals mg/m^3 in gas times 0.122 m^3/liter.

5.1.3 Fate of Inorganic Compounds in the Waste

The principal inorganic species which was found in the waste and known to be hazardous was cyanide ion at about 300 mg/l. As indicated in Table 5-2, the concentration of this species in the wet air oxidation process effluent was <3 mg/l. This corresponds to a destruction efficiency of >99%. The products of cyanide oxidation were not determined, but it was established that the cyanide was destroyed, and not merely stripped from solution as hydrogen cyanide. No hydrogen cyanide was detected in the vent gases leaving the scrubber.

Other inorganic constituents of the coke plant waste included chloride, sulfate and ammonia. The buffering action of the 3.6 g/l of ammonia is responsible for the fact that the pH of the process effluent was only slightly lower than that in the feed. Concentrations of chloride, sulfate and ammonia were unchanged in the wet air oxidation process (Table 5-2). Elements present in the waste at trace levels (1-10 ppm) were: potassium, 7 ppm; iron, 6.5 ppm; magnesium, 4 ppm; fluorine, 2 ppm; silicon, 2 ppm; and copper, 1 ppm. Calcium, sodium, and phosphorus were found at concentrations >10 ppm. None of these species is expected to be significantly affected by wet air oxidation and none of them is of concern at the concentrations present in the waste. The results of SEMS analysis (Appendix B) indicate that levels of trace metals in the effluent are the same, within experimental error, as in the feed. An exception to this statement is that copper, added as an oxidation catalyst, is present in the effluent at >200 ppm. This concentration is reduced to 2 ppm in a post-oxidation, catalyst-recovery step before the process effluent is discharged.

5.1.4 Potentially Hazardous Emissions

The potentially hazardous species known to be present in the aqueous process effluent were phenol at 1 mg/l, quinoline at 13 mg/l, cyanide at >3 mg/l and copper at 250 mg/l. Sulfide precipitation was found to be a technically feasible method for removal of the copper in a post-oxidation batch process.

No significant amounts of potentially hazardous particulate or vapor species appeared to be present in the vent gas. The 1000 ppm concentration of carbon monoxide in the vent gas, as shown by the on-line analyser, may require further emission controls under some local conditions. The total particulate loading of the vent gas was found to be 2.73 mg/m^3.

There was no evidence of significant contamination of the scrubber water.

5.2 RESULTS OF AMIBEN® WASTE TEST

5.2.1 Operating Conditions for Amiben® Waste Test

Operating conditions for the Amiben® waste test are summarized in Table 5-4. More detail is given in Appendix C.

5.2.2 Fate of Organic Components of the Waste

Analysis of the waste actually tested indicate that it contained 20.8 g/l of organic material, with two isomers of dichloronitrobenzoic acid as major components (Table 5-5. The 2,5-dichloro-3-nitrobenzoic acid, ("DINOBEN")** which was found at a concentration of 3.1 g/l, is reported* to be toxic: LD_{50} (oral, rat) = 3500 mg/kg of body weight. The other major waste component was 2,5-dichloro-6-nitrobenzoic acid, at a concentration of 16.0 g/l. In the absence of specific toxicity data, it is presumed that this species has a toxicity comparable to that of the 3-nitro isomer. The only other specific organic compound identified in the waste was a small amount (0.06 g/l) of dichloronitrobenzene. The fate of the dichloronitrobenzoic acids was selected as the major criterion for evaluation of wet air oxidation of the Amiben® waste.

Dichloronitrobenzoic acids could not be detected in the effluent from the wet air oxidation process. Since the detection limit for these species was 0.1 g/liter, the efficiency of destruction of the two dominant waste components can be estimated at 99.4%.

However, not all of the dichloronitrobenzoic acid destroyed is converted to carbon dioxide. The effluent from the wet air oxidation process contains 2.1 g/l of dichloronitrobenzene. This corresponds to 13.5% of the original quantity of dichloronitrobenzoic acid. The dichloronitrobenzene has a reported toxicity (LD_{50} [oral, rat] = 1200 mg/Kg) which is somewhat higher than that reported for the corresponding 3-nitrobenzoic acid, so formation of this product is not a desirable result. However, the dichloronitrobenzene can be removed from the process effluent by extraction with perchloroethylene before discharge of the treated waste to the municipal treatment plant. In these tests, a three stage perchloroethylene extraction removed >99% of the dichloronitrobenzene from the process effluent.

*"Registry of Toxic Effects of Chemical Substances," 1975 Edition, U.S. Department of Health, Education and Welfare, Rockville, Maryland, 1975.

** Trademark of Rorer-Amchem, Inc., Philadelphia, Pa.

TABLE 5-4

OPERATING CONDITIONS FOR TESTS ON AMIBENP WASTE

Waste Feed Rate	14.2 liters/hr (6.4 gph)
High Pressure Air Feed Rate[a]	2.86 cu m/hr (1.7 cfm)
Catalyst Addition Rate	1.1 liter/hr (0.3 gph)
Reactor Residence Time	~ 1 hr
Reactor Temperature	281°C (538°F)
Reactor Pressure	107 atm (1560 psig)
Effluent Gas Vent Rate	2.86 cu m/hr (1.7 cfm)

[a]ADL calculated value.

TABLE 5-5

PRINCIPAL COMPONENTS OF FEED AND EFFLUENT AQUEOUS STREAMS FOR AMBERS® WASTE TESTS

Component	Concentration, g/l	
	Feed	Effluent
Organic Species		
2,5-Dichloro-3-nitrobenzoic acid	3.1	--
2,5-Dichloro-6-nitrobenzoic acid	16.0	--
Total	19.1	N.D.(<0.1)
2,5-Dichloronitrobenzene	0.06	2.10
Inorganic Species		
pH	12.1	3.0
Cl^-	5.67	4.94
NH_3-N*	0.193	0.148
Collective Parameters		
BOD*	5.28	0.905
COD*	30.5	2.92
Total Solids*	54.83	36.3

* Asterisks indicate data reported by Zimpro, Inc. Others are ANL Values.

The 80.5%, or 16.5 g/l, of dichloronitrobenzoic acids which is not converted to dichloronitrobenzene appears to undergo complete oxidation to CO_2 (and some CO) and other inorganic species. Evidence for this includes:

- Absence of any significant amounts of other identifiable organic species in the aqueous effluent (Appendix B);
- Reduction of COD and BOD levels in the effluent to 9.6% and 17.1%, respectively, of the levels in the waste feed (Table 5-5);
- The vent gas from the reactor contains only low levels of hydrocarbons; and
- The vent gas contains levels of carbon dioxide and carbon monoxide which are more than sufficient to account for all of the carbon in the 16.5 g/l of dichloronitrobenzoic acid.

The later two statements may be clearer after examination of Table 5-6. In that table, the results of the on-line instrumental analyses of the vent gas are corrected to reflect the relative flow rates of vent gas and aqueous waste. The total quantity of carbon corresponding to the measured gaseous species is 7.23 g/l; 16.5 g/l of dichloronitrobenzoic acid corresponds to 5.87 g/l of carbon. The excess carbon in the vent gas is presumed to be due to inorganic carbonate initially present and stripped off as the pH was reduced.

In mass spectrographic analysis of the gas bulb sample, no hydrocarbon components were found to account for the 750 ppm as methane measured in the vent gas by the on-line analyser. One hypothesis which would explain the fact that these compounds were not detected is that they were very polar oxygenated species such as formaldehyde which were lost to the water droplets in the sampling bulb.

5.2.3 Fate of Inorganic Components of the Waste

There appear to be no significant differences between the waste feed and the oxidized effluent in terms of inorganic chemical composition. Potassium, sodium, chlorine and sulfur are major components in both feed and effluent and specific analyses show that the concentrations of sodium, chloride and sulfate are unchanged during oxidation. The results of SEMS analysis (Appendix B) indicate that the only trace elements present in the waste at concentrations >1ppm were: calcium, 44ppm; iron, 13ppm; phosphorus, 12ppm; silicon, 4ppm; titanium, 3ppm; fluorine, 2ppm; and iodine, 2ppm. None of these species is expected to be significantly affected by the wet air oxidation process and none of them is especially toxic at the concentrations present in the waste. The results of the SEMS analyses show that the levels of these trace elements in the

TABLE 5-6

CARBON-CONTAINING SPECIES IN VENT GAS FROM AMBIENT TEST

	Concentration in Vent Gas		Equivalent Concentration in Aqueous Waste Stream*	
	ppm	mg/m^3	mg/l	as Carbon mgC/l
Hydrocarbons (as methane)	730	550	65	49
Carbon Monoxide	1210	1511	420	180
Carbon Dioxide	1.2×10^6 (1.2%)	2.16×10^3	25.7×10^3	7.00×10^3
			Total	7.23g/liter

* Equivalence based on approximate total flows of 7.87 m^3/hr of vent gas and 24.2 l/hr of aqueous waste. Therefore, mg/l in waste equals mg/m^3 in gas times 0.119 m^3/liter.

process effluent are the same, within experimental error, as in the feed. An exception to this statement is that copper, added as an oxidation catalyst, is present in the effluent at about 300 ppm. The copper concentration is reduced to < 0.2 ppm in a post-oxidation, catalyst recovery step before the process effluent is discharged.

The dramatic decrease in pH between feed and effluent is typically observed in wet air oxidation of unbuffered solutions. In the case of Amiben® waste, the increase in acidity could be due to the production of nitric acid, although analyses were not performed to confirm this.

A somewhat surprising result of this test is that the concentration of free chloride ion does not increase above the ~ 5 g/l found in the feed to correspond to the destruction of the dichloronitrobenzoic acid. The 16.5 g/l of acid, which appeared to undergo complete oxidation to carbon dioxide, should have released 4.9 g/l of chlorine in some form. Analyses by Zimpro, Inc., involving vigorous sample digestion prior to analysis indicated that the total chlorine concentration of both feed and effluent is 10.9 g/l, so the chlorine released by oxidation is apparently remaining in solution. The possibility that substantial quantities of chlorinated organic species remain in solution but were not detected in any of the analyses is remote. At present, no conclusion can be drawn as to the speciation of the chlorine released by oxidation of dichloronitrobenzoic acid in these tests.

5.4 POTENTIALLY HAZARDOUS EMISSIONS

The aqueous process effluent from the Amiben® waste test is potentially hazardous due to the presence of 2.1 g/l of dichloronitrobenzene and of 300 ppm of copper. Both of these species would have to be removed before the oxidized waste would be suitable for discharge. During these tests, technically feasible methods for removal of each species in post-oxidation batch processes were demonstrated.

No potentially hazardous species appeared to be present in the comprehensive sampling train gas grab sample. The principal hazard identified in the vent gas was the high concentration of carbon monoxide of > 3000 ppm. Consequently, emission of the vent gas in a manner compatible with stationary or ambient air standards would be required. The total particulate loading of the vent gas was found to be 10.6 mg/m^3, of which 1% was organic solvent extractable.

There was no evidence of significant contamination of the scrubber water.

6. WASTE DESTRUCTION COSTS

Individual economic analyses have been developed for the destruction of coke plant and Amiben® wastes. The quantity of each type of waste to be destroyed is based upon the following estimates of waste generation from single sources:

	Size of Production Unit	Estimated Waste Flow to be Treated
Coke plant waste	3200 tons coke/day	2,120 cu m/day (560,000 gal/day)
Amiben® waste	"	151 cu m/day (40,000 gal/day)

The resulting liquids from wet-air oxidation of coke plant and Amiben® wastes must be treated further. Zimpro, Inc. finds that the degradation obtained in the wet-air oxidation process is usually such that biological treatment or activated carbon adsorption is useful in further reducing the pollutant. Often biologically toxic substances are broken down to intermediates which are no longer toxic to microorganisms or the concentrations are sufficiently lowered so as to cause no problems. On this basis, ADL has estimated the cost of the following treatment sequences to achieve satisfactory effluents.

Coke plant waste	Wet-air oxidation (including catalyst recovery) Ammonia removal Neutralization Biological treatment
Amiben® waste	Wet-air oxidation (including catalyst recovery and solvent extraction) Neutralization Biological treatment

As shown in Tables 6-1 and 6-3 the operating costs are approximately $10/cubic meter ($38/1000 gal) for coke plant waste and $18/cubic meter ($69/1000 gal) for Amiben® waste.

6.1 CAPITAL INVESTMENT

The Zimpro wet-air oxidation process has been used successfully in full scale destruction facilities for a number of domestic and industrial wastes. The actual test runs monitored were performed in a test trailer with equipment much smaller in size than would be used in actual facilities for these wastes. In preparing the capital investments which follow,

preliminary designs for a system to handle the specified flow rates were prepared.

Zimpro, Inc., provided estimates of the capital investment requirements for the wet-air oxidation treatment systems which included high pressure pumps, exchangers, reactors, pressure reducing valves, gas-liquid separators, catalyst recovery and the associated instrumentation.

The cost of the other equipment such as waste storage and ammonia stripping were estimated by ADL using cost data reported in the literature[1], updated using the Marshall and Swift Equipment (M&S) Index of 460 for March 1976.

The cost included for follow-up biological treatment has been presented as an operating cost in these estimates.

Our estimate of capital investment requirements appear in Tables 6-1 6-2 and 6-3.

6.2 OPERATING COSTS

The operating costs for treating coke plant and Amiben® wastes are presented in Tables 6-1 and 6-2. The operating costs are summarized below:

Waste	Amount treated (cu meters/yr)	Operating cost ($/cu meter)
Coke plant waste	700,000 (184.8 MM gal/yr)	11; ($38/1000 gal)
Amiben® waste	50,000 (13.2 MM gal/yr)	18 ($69/1000 gal)

Three full-time operators would be required for the coke plant waste since it would require two 200 gpm units and ammonia stripping. The Amiben® waste could be treated by having two operators full time. Although the oxidation treatment is smaller, the addition of an extraction step will be necessary. Power and supplemental heat requirements for the equipment used in these estimates were supplied by Zimpro, Inc. Fuel requirements in full scale units are based on an estimate of an heat available from the oxidation of the specific wastes. The waste in the full scale oxidation is pumped through an exchanger where the temperature is increased to the point at which the reaction takes place on its own. The heat released by the reaction is used to preheat the incoming waste stream. Zimpro, Inc. has determined that for a waste to become thermally self-sustaining in the wet oxidation in full scale equipment requires a COD of approximately 15,000 ppm. Amiben® waste would be above this COD level; the coke plant waste would not. In the pilot scale tests, the heat losses were so great that all of the heat had to be added from external sources.

[1] K.M. Guthrie, Process Plant Estimating Evaluation and Control, Craftsman Book Co. of America, Solano Beach, California (1974).

TABLE 6-1

OPERATING COST FOR WET OXIDATION TREATMENT
OF COKE PLANT WASTE

Basis: Fixed Capital Investment (FCI) $10.7 MM*
2120 cubic meters/day (560,000 gal/day) waste
Operation 24 hrs/day; 330 days/yr.
90% COD Reduction in Wet Oxidation
280°C, 1700 psig

	$/Unit	Units per cubic meter waste	$ per cubic meter waste	Annual cost ($)
VARIABLE COSTS				
Oil or gas	1.00/MM Btu	0.52 MM Btu	1.04	728,100
Electricity	0.015/kwh	11.3 kwh	0.17	119,000
Cooling water	0.008/cu m	4.2 cu m	0.03	35,100
Chemicals**			0.29	200,900
Operating labor	7/hr 2 men/shift			111,000
Supervision	15% operating labor			16,700
Labor Overhead	30% labor and supervision			38,300
Plant Overhead	70% labor and supervision			89,450
Maintenance	4% FCI/yr***			428,300
Total Variable Costs				1,765,900
FIXED COSTS				
Depreciation	(15% FCI/yr)			1,605,000
Cost of Capital	(10% FCI/yr)			1,070,000
Taxes and Insurance	(2% FCI/yr)			214,000
Total Fixed Costs				2,889,300
Total operating cost for wet oxidation				4,654,300
Additional operating cost for follow-on treatment****				2,242,000
Total cost of treatment				26,84x,000

TABLE 6-2

Footnotes

* Includes 2 days of storage capacity
** $ 45,000 catalyst replacement ($1.46/lb Cu equivalent)
$155,000 sodium sulfide for catalyst recovery ($250/ton); 1.8 lb/cu meter effluent
*** ADL estimate
**** Ammonia stripping $2,112,000 annually (see Table VI-2).
Neutralization and Biological treatment $130,000 annually.

TABLE 6-2

OPERATING COST FOR AMMONIA STRIPPING
OF OXIDIZED COKE PLANT WASTE

Basis: Fixed Capital Investment (FCI) $1,600
2120 cubic meters/day (560,000 gal/day) oxidized waste
Operation 24 hrs/day; 330 days/yr.

	$/Unit	Units per cubic meter oxidized waste	$ per cubic meter oxidized waste	Annual cost ($)
VARIABLE COSTS				
Steam	4/1000 lb	520 lb.	2.11	1,477,600
Electricity	0.015/kwh	0.45 kwh	0.007	4,600
Cooling water	0.008/cu m	12 cu m	0.10	70,000
Operating Labor	7/hr	4 m-h/shift		27,700
Supervision	15% operating labor			4,200
Labor overhead	30% labor and supervision			9,400
Plant overhead	70% labor and supervision			22,300
Maintenance	4% FCI/yr			64,000
Total Variable Costs				1,680,000
FIXED COSTS				
Depreciation (15% FCI/yr.)				240,000
Cost of Capital (10% FCI/yr)				160,000
Taxes and Insurance (2% FCI/yr)				32,000
Total Fixed Costs				432,000
Total Operating Cost				2,112,000

Source: ADL estimates

TABLE 6-3

OPERATING COSTS FOR WET OXIDATION
TREATMENT OF ACRYLIC WASTE

Basis: Fixed Capital Investment (FCI) $2.2 MM*
151 cubic meters/day (40,000 gal/day) waste
Operation 24 hrs/day; 330 days/yr.
91% COD Reduction in Wet Oxidation
260°C, 1700 psig

	Basis	Units per cubic meter waste	$ per cubic meter waste	Annual cost ($)
VARIABLE COSTS				
Oil or gas	2.00/MM Btu	0.26 MM Btu	0.52	26,000
Electricity	0.015/kwh	36.6 kwh	0.55	27,400
Cooling water	0.008/cu m	0.3	0.002	100
Chemicals**				30,000
Operating labor	$7/hr., 2 man/shift			55,370
Supervision	15% operating labor			8,300
Labor overhead	30% labor and supervision			19,100
Plant overhead	70% labor and supervision			44,700
Maintenance	4% FCI/yr.***			88,000
Total Variable Costs				344,106
FIXED COSTS				
Depreciation	(15% FCI/yr)			330,000
Cost of Capital	(10% FCI/yr)			220,000
Taxes and insurance	(2% FCI/yr)			44,000
Total Fixed Costs				594,000
Total Operating cost for wet oxidation				893,100
Additional operating cost for follow-on treatment ***				15,000
Total cost of treatment				$908,100

TABLE 6-3 (continued)

Footnotes

* Includes 5 days of storage capacity
** $3,200 catalyst replacement ($1.44/lb Cu equivalent)
$11,800 sodium sulfide for catalyst recovery ($250/ton);
$15,000 solvent extraction solvent makeup ($0.17/lb)
*** ADL estimate
**** Neutralization and Biological Treatment $15,000 annually.

7. CONCLUSIONS

Consideration of the results of these tests and operating characteristics of wet air oxidation systems results in the following conclusions being reached.

7.1 GENERAL

7.1.1 Waste Characteristics

Wet air oxidation is particularly well suited to the treatment of aqueous wastes containing a few percent or less of oxidizable contaminants.

7.1.2 Potential For Environmental Emissions

Emissions to the atmosphere from wet air oxidation is generally not of significant consequence of within established regulations. Aqueous effluents from wet air oxidation often can be expected to require further treatment to meet effluent limitations. Consequently, wet air oxidation systems may require minimal attention to air emissions, but will usually require subsequent water treatment for the removal of oxidation catalyst and/or the removal of residual organic substances.

7.1.3 Process and Economic Considerations

As a method of thermal destruction for chemical wastes, wet air oxidation has established a position based on its ability to treat wastes which are beyond the capabilities of the conventional biological and physiochemical systems but which cannot be economically destroyed by temperature incineration. Wet air oxidation is usually not a single step treatment system; however, it is an important technology which often can be incorporated into waste treatment systems to give an overall desirable combination of technology and economics.

7.2 COKE PLANT WASTES

7.2.1 Destruction of Waste Feed Components

The test showed >99% destruction of phenol, cresol and cyanide in the waste, 98.9% reduction in BOD, and 91.3% reduction in COD. Destruction efficiency for quinoline in the waste was 66%.

7.2.2 Potential for Environmental Emissions

The aqueous streams from wet air oxidation contained 13 ppm of quinoline, 250 ppm copper and 2410 ppm of ammonia (as N). Removal of copper would certainly have to be achieved prior to discharge of oxidized waste to receiving waters. The removal of residual organics and ammonia would

probably also be required; a number of methods such as activated carbon adsorption, ammonia stripping, and so on, might be considered.

The vent gases from the scrubber, containing 180 ppm hydrocarbons and 1057 ppm carbon monoxide, can probably be emitted to the atmosphere through a stack of sufficient height so as to prevent exceeding ambient air quality standard.

7.2.3 Process and Economic Considerations

Treatment of coke plant waste using wet air oxidation would require further treatment of the resulting liquid. In our test we did not attempt to perform these follow-on steps. Process effluents were sampled before and after the catalyst recovery operation. In full scale operation, we anticipate the need of ammonia removal (perhaps using steam stripping because of the relatively high level of ammonia in the raw waste), neutralization and biological treatment. The neutralization is necessary because ammonia removal is performed best on alkaline streams but these would not be suitable for biological treatment. The presence of copper in the effluent should be monitored so as not to exceed recommend levels. It is estimated that the cost of treatment (including the treatment steps which follow wet air oxidation) will be approximately $10/cubic meter ($38/1000 gal) for coke plant waste.

7.3 AMIDENO WASTES

7.3.1 Destruction of Waste Feed Components

The test showed >99.4% destruction of the 3-nitro plus 6-nitro isomers of 2,5-dichloronitrobenzoic acid, 90.4% reduction in BOD and 87.9% reduction in COD. However, 13.5% of the dichloronitrobenzoic acid was accounted for by dichloronitrobenzene in the process effluent.

7.3.2 Potential for Environmental Emissions

The aqueous stream from wet air oxidation contained 2100 ppm of 2,5-dichloro nitrobenzene, 300 ppm copper and 150 ppm of ammonia (as N). The 2,5 dichloro nitrobenzene could be removed by perchloroethylene extractions; however, subsequent treatment for removal of copper, residual organics, and ammonia would probably be required as for the coke plant waste. The vent gases from the scrubber containing 750 ppm hydrocarbons and 3210 ppm carbon monoxide can probably be emitted to the atmosphere directly through a stack of sufficient height so as to prevent exceeding ambient air quality standards or could be oxidized by thermal or catalytic means.

7.3.3 Process and Economic Considerations

The liquid effluent from wet-air oxidation treatment of Amiben® waste must be treated further. It is anticipated that solvent extraction will be necessary to remove decarboxylation products and that neutralization and biological treatment will be necessary because of the acidic nature of the oxidized waste and its BOD and COD values which are greatly reduced during treatment but are still relatively high. In the test run wet-air oxidation and solvent extraction were performed. The estimated cost of treatment (including the treatment steps which follow wet-air oxidation) is approximately $18/cubic meter ($69/1000 gal) for Amiben® waste.

APPENDIX A

TECHNIQUES OF SAMPLE PREPARATION AND ANALYSIS

A.1 Extraction of Collected Samples

A.2 Analytical Methods for Organic Materials

A.3 Analytical Methods for Inorganic Materials

A.4 Analyses of Gaseous Effluents

A.5 Sources for Spark Source Mass Spectrometry and Gas Bulb Analyses

APPENDIX A

TECHNIQUES OF SAMPLE PREPARATION AND ANALYSIS

A.1 EXTRACTION OF COLLECTED SAMPLES

A.1.1 Coke Plant Waste Test - Aqueous Samples

Measured volumes of composited samples of waste feed, process effluent, scrubber water feed and scrubber water effluent were extracted with equal volumes of methylene chloride in a separatory funnel. This procedure was repeated at acidic, basic and neutral pH's. Sulfuric acid or sodium hydroxide were used in adjusting pH to 1 or 11, respectively. The weights of extractable material were determined by drying to constant weight at ambient temperature.

A.1.2 Amiben® Waste Test - Aqueous Samples

Measured volumes of composited samples of waste feed, scrubber water feed, and scrubber water effluent were extracted with equal volumes of diethyl ether. This procedure was repeated at acidic, basic and neutral pH's. (See above.)

The aqueous process effluent was subjected to two different extraction procedures. In the first extraction, the thin film of material which oiled out of the aqueous effluent was removed by shaking one liter of effluent with 200 ml of pentane. The remaining aqueous layer was then extracted twice each with diethyl ether at acidic basic and neutral pH's. The weights of ether and pentane extractable materials were determined by drying to constant weight at ambient temperature. The second extraction procedure was chosen to simulate the batch treatment applied by Zimpro, Inc., to the composite process effluent. A measured value of process effluent sample that had been freshly thawed after freezer storage was extracted with 1/3 its volume of perchloroethylene with no adjustment of pH. The procedure was repeated until no color was observed in the organic layer.

A.1.3 Filter from Comprehensive Sampling Train

The filter was placed in a pre-cleaned Soxhlet thimble and extracted for 24 hrs. with methylene chloride. The extract was evaporated to dryness at ambient temperature and the total mass of extracted material determined.

A.1.4 Sorbent Trap from Comprehensive Sampling Train

The sorbent trap was fitted into the specially designed extraction apparatus shown in Figure A-1 and extracted for 24 hours with pentane then for 24 hours with methanol. The two extracts were combined, evaporated to dryness at ambient conditions, and the total mass of extracted material was determined.

A.2 ANALYTICAL METHODS FOR ORGANIC MATERIALS

A.2.1 Gas Chromatography (GLC)

A.2.1.1 Coke Plant Waste Tests

The methylene chloride extracts of the coke plant samples were analysed quantitatively for phenol, aniline, cresol, napthalene, indole and quinoline. Standard curves were drawn for each of the compounds. Peaks were identified by cochromatography and GC-MS.

These analyses were done in ADL laboratories on a Varian Model 3700 gas chromatograph with a flame ionization detector. The column was 3% Dexsil® 400 on 100/120 mesh Supelcoport®*, and the temperature was held at 50°C for 3 min.; then programmed to 350°C at 10°/min. The detector response was integrated automatically with an Autolab System I integrator.

A.2.1.2 AMIBEN®

The ether and perchloroethylene extracts of the Amiben® samples were analysed quantitatively for 2,5-dichloronitrobenzene. The same system used for coke plant waste was used for Amiben®, except that the samples were temperature programmed from 70°C to 150°C, at a rate of 10°C per minute. The integrated areas of the samples were compared to known standards of dichloronitrobenzene and the masses determined. Peaks were identified by cochromatography.

A.2.2 High Performance Liquid Chromatography (HPLC)

HPLC was used to quantitatively analyse dichloronitrobenzoic acid in Amiben®-Feed and wet oxidation effluents. The analyses were done using a Waters Associates Model 201 HPLC System incorporating a Model 6000A solvent delivery system and a Model 440 absorbance detector, 254 nm. The aqueous samples were introduced, using a Model U6K universal LC injector, into a Whatman Partisil 10/25 (10 micron silica) column and eluted with $CHCl_3$/MeOH/H_2O, 48:13:0.8. The areas under the peaks were taken with a planimeter and the weight they represented was read from standard curves made for 2,5-dichloro-3-nitrobenzoic acid and 2,3-dichloro-6-nitrobenzoic acid. LC peaks were identified by cochromatography.

A.2.3 Infrared Spectroscopy (IR)

Extracts and rotary evaporation residues of Amiben® and coke samples were examined as potassium bromide micro-pellets. Analyses were done in ADL's laboratories using a Perkin-Elmer Model 521 Grating Infrared Spectrophotometer.

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* Trademark of Supelco, Inc.

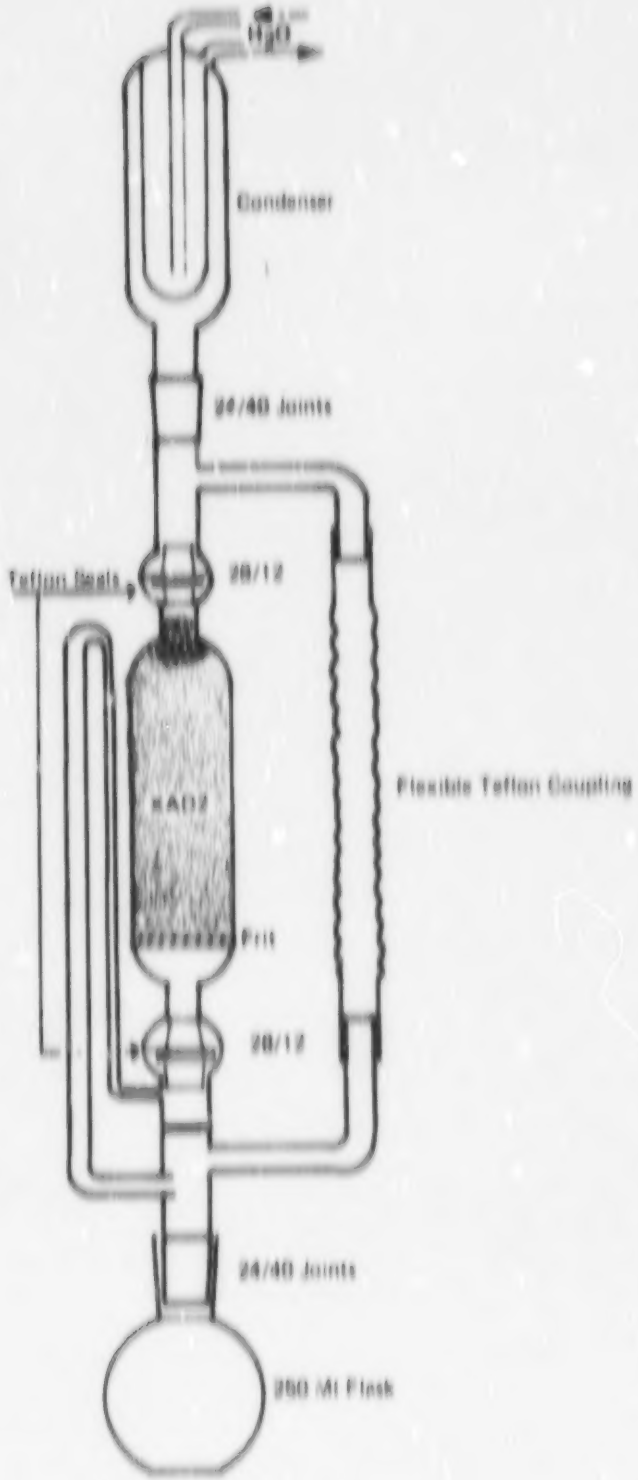

Figure A-1. Sorbent Trap Extractor

A.2.4 Low Resolution Mass Spectroscopy (LRMS)

The extracts and vacuum flash evaporation residues of coke and Amiben® samples were subjected to LRMS studies. These analyses were performed in ADL's laboratories using a DuPont (CEC)21-110B high resolution mass spectrometer, with sample introduction by a glass inlet or a solid probe.

A.2.5 Gas Chromatography - Mass Spectroscopy (GC-MS)

Extracts of coke waste samples were chromatographed as neat and trimethylsilylated samples on a 3% OES 400 column. The individual GLC peaks were subjected to MS analysis via a jet interface. These analyses were done in ADL's laboratories using a Hewlett Packard 5700A Gas Chromatograph interfaced with a DuPont 21-491 Mass Spectrometer and Hewlett Packard 2100 computer.

A.3 ANALYTICAL METHODS FOR INORGANIC MATERIALS

A.3.1 pH Determinations

The pH of coke and Amiben® composited feed and effluent samples were taken in ADL laboratories using a Beckman pH meter with an Orion single junction reference electrode and a Corning pH triple purpose electrode. The samples were constantly mixed with a Teflon®magnetic stirrer on a stirring plate.

A.3.2 Atomic Adsorption Spectroscopy

Composited aqueous samples of Amiben® and coke were analysed for copper using a P-E 303 AA with a background corrector, concentration mode ten-second integration.

A.3.3 Titration Methods

Chloride analyses of aqueous coke and Amiben® samples were done by titration with $Hg(NO_3)_2$, after first oxidising the sample and precipitating $SO_4^=$ with $Ba(NO_3)_2$.

Sulfate analyses were done with a Barium Chloranilate titration method. A check was done using the $Pb(ClO_4)_2$ titration which agreed within 1%.

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A.4 ANALYSES OF GASEOUS EFFLUENTS

A.4.1 On-Line Instruments

A continuous recording was made of the output of each of the five on-line instruments. In reducing the data, readings were made from the charts at 10 minute intervals and the values averaged.

The instruments were calibrated (zero and span) at least every two hours using the following gases (supplied with analyses by Matheson Gas Products Company).

Analyzer	Zero Gas	Span Gas	
Hydrocarbons	air	40 ppm C_3H_8 in N_2	These were combined in one cylinder.
Carbon Monoxide	air	138 ppm CO	
Carbon Dioxide	air	12.4% CO_2	
Nitrogen Oxides	air	432 ppm NO in N_2	
Oxygen	CO, CO_2, C_3H_8 span gas	air	

It is estimated that the error introduced by use of span gas concentrations different from the measured sample gas concentrations (for hydrocarbons and carbon monoxide) would be no more than 10%.

A.4.2 Gas Detecting Tubes

Bendix Gastec® tubes number 12L, Hydrogen Cyanide, Low-Range, (½-5-60 ppm) were used with a Bendix® hand sampling pump.

® Trademark of Bendix Environmental Science Division

A.5 SOURCES FOR SPARK SOURCE MASS SPECTROMETRY AND GAS BULB ANALYSES

A.5.1 Spark Source Mass Spectrometry

Commercial Testing & Engineering Co.
Instrumental Analysis Division
14335 W. 44th Avenue
Golden, Colorado 80401

For these wastes the rotary evaporation residues of the coke and feed samples and effluent samples were submitted.

A.5.2 Mass Spectrometry of Gas Bulb Samples

Galiub Analytical Service Corporation
47 Industrial Road
Berkeley Heights, New Jersey 07922

APPENDIX B

SAMPLING AND ANALYTICAL RESULTS

B.1 Sampling Data

B.2 Results of Analyses of Samples from Coke Waste Test

B.3 Results of Analyses of Samples from Amiben® Waste Test

B.4 Results of Analyses by Kimpro, Inc.

8.1 SAMPLING DATA

The volumes of vent gas samples by the comprehensive sampling train, corrected to STP were:

	Coke Waste Test	Amiben® Test
Measured Dry Volume, m^3	3.931	3.913
Moisture Content	1.7%	2.0%
Calculated Volume of Water Vapor, m^3	0.066	0.079
Total Sample Volume, m^3	3.997	3.992

No attempt was made to sample isokinetically because of the small diameter (≈ 2") of the vent pipe and the low total flow (≈ $3m^3$/hr) of the vent gas.

8.2 RESULTS OF ANALYSES OF SAMPLES FROM COKE WASTE TEST

8.2.1 Waste Feed

8.2.1.1 Gravimetric Analysis

Evaporation of a one-liter aliquot of waste to dryness on a rotary evaporator with gentle heating (≈ 50°C) gave 9.670 g/l of residue.

Extraction of the waste with methylene chloride at acidic, basic and neutral pH's gave a combined organic extract containing 0.25 g of solute per liter of extracted waste. A control experiment using water spiked with phenol showed that recovery of that species by this procedure was low. Since phenol was found to be a major organic component of the waste, the residue from gravimetric analysis of the organic extract was not used for quantitative analysis of organics.

8.2.1.2 Analysis of Organics

The IR spectrum of the residue remaining after rotary evaporation of a waste aliquot showed mainly inorganic components: NH_4^+, $SO_4^=$, CN^- and some NO_3^-.

The LRMS of an unconcentrated sample of coke waste revealed the presence of phenol and cresol. Attempts to concentrate the sample by vacuum evaporation or concentration of a methylene chloride extract apparently resulted in loss of these two major components. The LRMS analyses of concentrated extracts showed small quantities of a variety of heterocyclic aromatics such as benzimidazole. Direct GC/MS analysis of a methylene chloride extract that had not been concentrated by evaporation showed: phenol, 2 isomers of cresol, dimethyl phenol (2 isomers), quinoline and indole. Quantitative analysis of the unconcentrated methylene chloride extract by GC showed concentrations of: phenol, 533 mg/l; and aniline, 26 mg/l. (The aniline could not be resolved from the phenol in the GC/MS run.)

8.2.1.3 Analysis of Inorganics

Analysis of a sample of waste feed showed a sulfate concentration of 970 ppm as sulfur and a chloride concentration of 0.356% or 3.56 g/l. The pH of the waste was 8.6.

The results of SSMS analysis of the residue remaining after vacuum evaporation of an aliquot of waste are presented in Table A11-1. In order to correct the data in the table to give the concentrations in the waste it is necessary to multiply by 0.0097.* A concentration of 100 ppm in the residue corresponds to 1 ppm in the waste feed. The copper concentration was found by AA to be 0.5 ppm.

8.2.2 Aqueous Process Effluent

8.2.2.1 Gravimetric Analyses

Evaporation of a one-liter aliquot on a rotary evaporator gave a residue of 10.216 g/l. The combined methylene chloride extracts from acidic, basic and neutral extractions gave 0.10 g of extractable material per liter of effluent.

8.2.2.2 Analysis of Organics

The IR spectrum of the residue on evaporation showed NH_4^+ and $SO_4^=$. The LRMS of this residue showed a mixture of aromatic species, like that in the feed, at very low abundances.

*This is because the residue amounted to 0.97% by weight of the waste.

The LRMS of the methylene chloride extract showed small quantities of these species as well. The LRMS also showed evidence of phthalates, which are presumed to have been introduced as contaminants by the plastic plumbing used at Simpro.

The levels of phenol, cresol, indole and aniline in the process effluent were found to be <20 mg/l in the oxidised effluent by GC analysis of an unconcentrated methylene chloride extract of the waste. The high detection limit in this analysis is due to the fact that species such as phenol were shown to be lost if the extract was concentrated. Quinoline concentration was determined after extract concentration to be 13 mg/l in the process effluent.

B.2.2.3 Analysis of Inorganics

Analysis of a sample of aqueous process effluent showed a sulfate concentration of 950 ppm as S and a chloride concentration of 0.355% or 3.56 g/l. The pH of the effluent was 7.7.

The results of SSMS analysis of the residue remaining after vacuum evaporation of an aliquot of aqueous process effluent were presented in Table AII-1. In order to correct the data in that Table to give the concentrations in the waste it is necessary to multiply by 0.010.[A] A concentration of 100 ppm in the residue is equivalent to 1 ppm in the process effluent. The copper concentration was found by AA to be 135 ppm.

B.2.3 Gaseous Process Effluent (Vent Gas)

B.2.3.1 On-Line Instrument Data

Data reported are means and standard deviations of values read from the strip charts at 15 minute intervals during the 3 hour grab sample collection period.

Hydrocarbons:	180 ± 20 ppm
Carbon Monoxide:	1050 ± 35 ppm
Carbon Dioxide:	2.30 ± 0.15%
Nitrogen Oxides:	0.35 ± 0.05 ppm
Oxygen:	17.9 ± 0.3%

The Gas Tec® tube analyses showed no hydrogen cyanide in the effluent.

[A]This is because the residue amounted to 1.0% by weight of the waste.

TABLE 6-1

RESULTS OF SPMS ANALYSIS OF RESIDUES FROM COKE WASTE SAMPLES[a]

Element	Conc., ppm		Element	Conc., ppm	
	Feed	Effluent		Feed	Effluent
Calcium	MC[b]	MC	Gallium	3	0.6
Sulfur	MC	MC	Cobalt	3	8
Phosphorus	MC	33	Manganese	2	1
Sodium	MC	MC	Antimony	1	< 0.3
Potassium	130	970	Tin	1	≤ 0.6
Iron	700	70	Rubidum		
Magnesium	440	MC	Scandium	≤ 1	≤ 0.8
Fluorine	190	10	Cerium	0.7	≤ 0.2
Silicon	180	52	Bismuth	0.6	7
Copper	130	MC	Yttrium	0.9	≤ 4
Chlorine	81	6	Bromine	0.6	0.7
Titanium	72	23	Iodine	0.2	0.1
Aluminum	48	19	Beryllium	≤ 0.1	≤ 0.1
Zinc	442	37			
Germanium	34	0.4			
Strontium	23	9			
Chromium	20	7			
Boron	18	4			
Arsenic	11	≤ 0.8			
Lithium	10	5			
Molybdenum	6	9			
Nickel	4	5			
Lead	4	7			
Cadmium	3	2			
Vanadium	3	0.6			
Zirconium	3	2			
Barium	2	3			
Selenium	2	1			

[a] Concentration in residue should be multipited by 0.0097 (Feed) or 0.010 (Effluent) to obtain concentration in aqueous stream.

[b] MC = Major Component

8.2.3.2 Results of Gas Bulb Analyses

The results of analysis by Gollub Analytical Service Corp. of a grab sample collected from the bypass line of the hydrocarbon analyzer were:

Nitrogen	78 + 5 (v/v)
Oxygen	18.1
Argon	0.98
Carbon Dioxide	2.7
Hydrogen	ND (<0.0005)
C_1-C_5 Alkanes	ND (<0.01%)

The oxygen and carbon dioxide values are in good agreement with the results of the on-line instrument analyses. The fact that no hydrocarbon species were detected in the mass spectrometric analysis may imply that the hydrocarbon initially present is reactive and is lost in shipping and storage. An alternative explanation is that the hydrocarbon consists of very polar species such as formaldehyde which is dissolved in the water droplets present in the sampling bulb.

8.2.3.3 Comprehensive Sampling Train Gas Sample

The net weight gain of the particulate filter was 10.9 mg. This corresponds to 5.71 mg/m^3. The particulate material was not analysed for trace components. However, based on the characteristics of the wet air oxidation process and on the results of analyses of the aqueous effluent, it is improbable that any significant hazardous material was present in this sample.

The combined pentane-methanol extracts of the sorbent trap yielded 10 mg of extractable material. The LRMS analysis indicated that this sample contained anthracene, stilbene, phenyl napthalene, methyl anthracene, diphenyl thiophene and benzoic acid. These species are believed to be contaminants because the same constituents were also found in the sorbent trap from the Ambon® test in the same absolute and relative abundances. They also appeared in smaller concentrations in the LRMS of the extract of an unused sorbent trap which had been brought back from Kimpro as a control.

8.2.4 Scrubber Water Samples

Analyses of samples of water entering and leaving the vent gas scrubber showed no significant differences between the two:

	Scrubber Water	
	Inlet	Discharge
Density	0.997 g/ml	0.996 g/ml
Residue on Evaporation	0.190 g/l	0.196 g/l
Methylene Chloride Extractables	0.02 g/l	0.02 g/l
pH	7.4	7.2
Chloride	25 ppm	25 ppm
Sulfate	9 ppm	12 ppm

The near constant pH is particularly significant, indicating that volatile acids are not being emitted in the vent gas since if they were the discharge water would have had a low pH.

B.3 RESULTS OF ANALYSES OF SAMPLES FROM AMIBEN® WASTE TEST

B.3.1 Waste Feed

B.3.1.1 Gravimetric Analyses

Evaporation of a one-liter aliquot of water to dryness on a rotary evaporator with gentle heating (T < 30°C) gave 66.841 g/l of residue. This is somewhat higher than the value of 54.83 g/l of "total solids" obtained by Simpro, Inc., (Table B-4) and may indicate incomplete drying.

Extraction of the waste with diethyl ether at acidic, basic and neutral pH's gave a combined organic extract containing 2.4365 g of solute per liter of extracted waste. It was later found that the aqueous waste contained substantial quantities of organic acids which were not effectively extracted with ether. The 2.4 g/l is therefore not a realistic estimate of the "organic loading". The Simpro data imply an organic loading of 20.8 g/l (TOC-ash).

B.3.1.2 Analysis of Organics

The residue remaining after vacuum evaporation of the Amthem® waste feed sample was separated into a methanol soluble fraction and a methanol insoluble residue for IR analysis. The methanol soluble fraction showed absorption in the OH, NH stretching region, evidence of aromaticity at at 3100 cm^{-1} and aromatic substitution pattern bands in the 700-900 cm^{-1} region. The spectrum also revealed the presence of carboxylate, $C-NO_2$, an C-Cl functions.

This qualitative observation was supported by the results of HPLC analysis of the waste which showed that the concentrations of two isomers of dichloronitrobenzoic acid accounted for about 92% of the estimated total organic material. The concentrations found were 3.1 g/l of 2,5-dichloro-3-nitrobenzoic acid and 16.0 g/l of the corresponding 6-nitro isomer.

The LRMS of the residue obtained on vacuum evaporation of the waste showed dichloronitrobenzene as the major component. This product apparently was produced by decarboxylation of the corresponding benzoic acids in the inlet of the mass spectrometer. The same species was identified by GC/MS. Gas chromatographic analysis of an organic extract of the waste showed 0.062 g/l of dichloronitrobenzene. No other specific organic compounds were identified in any of the analyses of the waste feed.

B.3.1.3 Analysis of Inorganics

The survey analysis of a pre-test sample of the waste had shown sulfate and chloride as major inorganic constituents. Analysis of a sample of the actual waste feed showed a sulfate concentration of 1.29% or 4.44 g/l as sulfur and a chloride concentration of 0.55% or 5.67 g/l. The pH of the waste was 12.1.

The results of ASMS analysis of the residue remaining after rotary evaporation of an aliquot of waste are presented in Table B-2. In order to correct the data in the Table to give the concentrations in the waste it is necessary to multiply by 0.065.[a] A concentration of 16 ppm in the residue corresponds to 1 ppm in the waste feed. The copper concentration was determined by AA as 0.41 ppm.

B.3.2 Aqueous Process Effluent

B.3.2.1 Gravimetric Analyses

The density of the effluent was found to be 1.024 g/ml.

Evaporation of a one-liter aliquot to dryness on a rotary evaporator with gentle heating (< 30°C) gave 42.884 g/l of residue. This is again somewhat higher than the 36.1 g/l reported by Zimpro (Table B-4) and may indicate incomplete drying.

[a]This is because the residue was 6.5% by weight of the waste.

TABLE F-2

RESULTS OF SSMS ANALYSIS OF RESIDUES FROM AMIREX WASTE SAMPLES[a]

Element	Conc., ppm		Element	Conc., ppm	
	Feed	Effluent		Feed	Effluent
Potassium	MC[b]	MC	Bismuth	≤ 0.2	4
Chlorine	MC	MC	Barium	≤ 0.2	0.6
Sulfur	MC	MC	Tin	≤ 0.2	2
Calcium	650	280			
Iron	490	170			
Phosphorus	180	130			
Silicon	53	31			
Titanium	44	22			
Fluorine	~36	~5			
Iodine	24	0.2			
Manganese	7	4			
Aluminum	6	4			
Magnesium	5	100			
Bromine	5	0.9			
Zinc	9	10			
Arsenic	4	≤ 1			
Chromium	4	3			
Boron	2	0.4			
Lead	2	2			
Strontium	3	7			
Gallium	≤ 2	0.6			
Scandium	≤ 2	≤ 0.9			
Vanadium	1	≤ 0.6			
Copper	1	MC			
Rubidium	0.4	0.2			
Selenium	≤ 0.6	≤ 0.3			
Germanium	0.3	0.2			
Cobalt	0.9	1			
Lithium	0.2	≤ 0.1			

[a] Concentration in residue should be multiplied by 0.065 (Feed) or 0.042 (Effluent) to obtain concentration in aqueous stream.

[b] MC = Major Component

Extraction of the process effluent with pentane and ether after the sample had been standing for several weeks gave a total residue after evaporation of organic solvent of 0.7330 g per liter of aqueous effluent. This was considerably lower than the 1.71 ± 0.05 g/ℓ of material found by evaporation of the combined perchlorethylene extracts prepared by Zimpro shortly after the test. Another aliquot of the composite aqueous effluent was thawed at ADL and extracted with perchlorethylene. Analysis of the perchlorethylene extracts (Zimpro's and ADL's) by GC showed dichloronitrobenzene as the major component. The concentrations found corrected back to the process effluent, were 1.54 g/ℓ and 2.67 g/ℓ for a mean of 2.1 g/ℓ. Analysis of the ADL pentane and ether extracts implied only 0.3 g/ℓ of dichloronitrobenzene in the process effluent, which suggests that this product was being lost from the aqueous sample on standing.

The concentration of dichloronitrobenzoic acids in the aqueous process effluent was below the limits of detection of the HPLC analysis or <0.1 g/ℓ. No other organic species were identified as significant components of the aqueous process effluent. Dioctylphthalate, presumably from contamination by plastic plumbing, was detected in the pentane extract of the effluent by LRMS analysis. The LRMS of the residue on evaporation of an aliquot of the waste did show the presence of a small amount of a mono-chlorinated species with m/e of 200, but no structure could be reliably assigned.

8.3.2.2 Analysis of Inorganics

Analysis of a sample of aqueous process effluent showed a sulfate concentration of 1.22% or 4.18 g/ℓ as sulfur and a chloride concentration of 0.48% or 4.92 g/ℓ. The pH of the effluent was 1.1.

The results of the SSMS analysis of the residue remaining after rotary evaporation of an aliquot of effluent were presented in Table 8-2. In order to correct the data in the Table to give the concentrations in the effluent, it is necessary to multiply by 0.042.[a] A concentration of 24 ppm in the residue corresponds to 1 ppm in the effluent. The copper concentration in the effluent was found by AA to be 304 ppm.

8.3.3 Gaseous Process Effluent (Vent Gas)

8.3.3.1 On-Line Instrument Data

Data reported are means and standard deviations of values read from the strip charts at 15 minute intervals during the 1 hour grab sample collection period.

[a] This is because the residue was 4.2% by weight of the waste.

Hydrocarbons:	750 ± 20 ppm
Carbon Monoxide:	3210 ± 80 ppm
Carbon Dioxide:	12.0 ± 0.9%
Nitrogen Oxides:	12.3 ± 2.2 ppm
Oxygen:	9.1 ± 0.7%

8.1.3.2 Results of Gas Bulb Analyses

The results of analyses by Golluh Analytical Service Corp. of a grab sample collected from the bypass line of the hydrocarbon analyser were:

Nitrogen	>74% (v/v)
Oxygen	8.2%
Argon	0.85
Carbon Dioxide	15.6
Hydrogen	0.50
C_1-C_5 Alkanes	ND (<0.01%)

The oxygen and carbon dioxide data are in reasonably good agreement with the results of the on-line instrument analyses. It is somewhat surprising that the mass spectrometric analysis of the gas bulb sample did not reveal the identity of species responsible for the 750 ppm of hydrocarbon measured by the on-line analyser. If the hydrocarbons present were very polar, they may have dissolved in the water droplets in the sampling bulb.

8.1.3.3 Comprehensive Sampling Train Gas Sample

The net weight gain of the particulate filter was 42.3 mg corresponding to 10.6 mg/m^3. Of this total, 0.5 mg or 0.13 mg/m^3 was extractable with methylene chloride. The particulate material was not analyzed for these components. However, as in the case of the coke waste test, it is improbable that any significant hazardous material was present in this sample.

The combined pentane-methanol extracts of the sorbent trap yielded 48.4 mg of material. This material was shown by LRMS to contain the same mixture of aromatics found in the analogous coke waste sample, (anthracene, stilbene, phenyl napthalene, etc.). The species present may be contaminants since they are also found in the control sorbent trap.

B.3.4 Scrubber Water Samples

Analyses of samples of water entering and leaving the vent gas scrubber showed no significant differences between the two:

	Scrubber Water	
	Inlet	Discharge
Density	0.991 g/l	0.990 g/l
Residue on Evaporation	0.243 g/l	0.182 g/l
Diethyl Ether Extractables	0.020 g/l	0.020 g/l
pH	7.3	6.9
Chloride	30 ppm	35 ppm
Sulfate	15 ppm	25 ppm

In particular, the data show that no significant quantities of volatile acids were being emitted in the vent gas, since if they were the discharge water would have had a low pH.

B.4 RESULTS OF ANALYSES BY ZIMPRO, INC.

The data presented in Tables B-3 - B-6 were obtained by personnel at Zimpro, Inc.

In almost all instances where analyses were duplicated, the ADL and Zimpro results agree within a factor of two and usually within a few percent. One exception is the chloride data in Table B-4; these values are higher than ADL's numbers by a factor of about two for Ambien® feed and effluent. Zimpro digested the samples by sodium carbonate fusion or nitric acid digestion prior to analysis and presumably measured total chlorine; while ADL's procedure measured free chloride ion.

We have drawn on the Zimpro, Inc., data whenever appropriate to complement the results of ADL's analyses.

TABLE 6-1

ANALYSIS OF COKE PLANT WASTE FEED AND OXIDIZED LIQUORS

	Waste Feed	Composite Oxidized Waste	Decoppered Oxidized Waste
COD, g/l	5.52	0.481	0.543
BOD_5, mg/l	2083	23	10.5
Total Solids, g/l	5.71[ø]	8.56	8.55
Total Ash, g/l	0.61	2.0	1.29
Suspended Solids, g/l	0.08	0.06	0.042
Suspended Ash, g/l	0.02	0.01	--
pH	8.9	7.6	8.1
Color	3715	60	75
Soluble Hardness, ppm	19	--	--
Total Chloride, g/l	3.3	3.29	3.31
Soluble Chloride, g/l	3.3	3.3	3.3
Total Kjeldahl Nitrogen, g/l	2.63	2.77	2.52
Ammonia Nitrogen, g/l	2.41	2.58	2.53
Cyanide, ppm	309	< 1	< 1
Phenol, ppm	743	1.05	1.05
p-Cresol, ppm	188	< 0.1	0.21
Soluble Copper, ppm	--	225	2.1
Total Copper, ppm	--	244	2.1

ø This value appears to be in error

TABLE B-4

ANALYSIS OF AMIBENS WASTE FEED AND OXIDIZED LIQUORS

		Composite Oxidized Waste		
	Waste Feed	Reactor Effluent	Extracted Effluent	Decolorized Extracted Effluent
COD, g/l	30.5	2.92	2.70	2.45
BOD_5, mg/l	5285.5	905.4	864.4	1114.7
Total Solids, g/l	54.83	36.3	36.85	36.4
Total Ash, g/l	34.0	35.61	36.23	35.87
Suspended Solids, g/l	0.165	0.063	0.126	0.084
Suspended Ash, g/l	0.12	0.031	0.116	0.061
pH	12.1	3.0	3.1	3.8
Color	44,875	3,500	2,750	4,000
Soluble Hardness, ppm	--	--	--	--
"Total Chloride," g/l*	10.9	10.9	10.2	10.2
"Soluble Chloride," g/l**	5.0†	10.0	10.18	10.27
Total Kjeldahl Nitrogen, g/l	1.31	0.161	0.19	0.147
Ammonia Nitrogen, g/l	0.193	0.148	0.148	0.112
Total Sodium, g/l	12.09	12.62	12.4	
Soluble Copper, ppm	--	313.6	315.5	--
Total Copper, ppm	--	344.9	319.7	--
Nonvolatile Organics, g/l	--	2.79	0.40	0.30
% of Nonvolatile Organics as p-DCNB	--	47.66	11.50	2.40

* Determined following sodium carbonate fusion of sample.

** Determined following 5 min. digestion with boiling nitric acid.

† Value originally reported by Zimpro, Inc. as 10.06 g/l. The analysis was repeated and reported to give the value shown in the Table.

TABLE B-5

AVERAGE ANALYSIS OF VENT GASES FROM OXIDATION OF COKE PLANT AND AMIREN® WASTES

	Gases From Coke Plant Waste Oxidation		Gases From Amthen® Waste Oxidation	
	Before Scrubber	After Scrubber	Before Scrubber	After Scrubber
O_2, Vol. %	17	17.25	9.3	10.6
N_2, Vol. %	76.45	76.1	74.55	73.8
CO_2, Vol. %	1.85	2.06	11.40	11.5
CO, ppm	333	320.6	4463.5	4469
CH_4, ppm	2	1	5.9	5.34
Total Hydrocarbons (less methane), ppm	106	93	1174	516.34

TABLE 5-6

AVERAGE SCRUB LIQUOR ANALYSIS

	Coke Plant Waste Oxidation	Amthen® Waste Oxidation
pH	7.5	7.6
COD, mg/l	12,30	214,55
Total Kjeldahl Nitrogen, mg/l	6,70	2,3
Ammonia Nitrogen, mg/l	< 1	< 1

APPENDIX G
OPERATING DATA

TABLE C-1

PROCESS DATA FOR JOE PLANT WASTE TEST

DATE 4.27.76

Time	Flow Rates: Waste Fuel GPH	Heat GPH	Catalyst Addition GPH	Liquid Effluent GPH	H.P. Air Addition: Heater	H.P. Air Addition: Reactor 1	Excess O_2 %	Pressures, psig: H.P. Air PI-1	Waste Feed PI-2	Catalyst Feed PI-3	Reactor 2 Outlet PI-11
					Avg. 2.55 cu ft/hr (1.52 x 3a)						
1500	4.5	85.3	–				19.5	1850	1560	1630	1540
1600	4.0	77.6	–				18.2	1850			1540
1700	4.5	98.9	–	5.95			18.3	1960			
1825	5.5	82.5	0.3	6.2			17.5	1960			
1900	6.0	79.4	0.3	6.1			17.3	1960			
2000	6.0	85.5	0.3	6.0			17.2	1960			
2100	–	96.2	0.3	6.0			17.1	1960	"		
2200	6.75	90.7	0.3	6.0			17.0	1965	1555		
2300	–	–	0.3	6.0			17.2	1960	1540	"	
2400	5.85	93.1	0.3	6.5			17.5	1960		1620	"
0100	6.0	87.0	0.3	6.3			17.2	1960			1550/1580
0200	6.0	89.0	0.3	6.5			17.5	1960			1540/1620
0300	5.0	86	0.3	6.1			17.5	1960			1540/1560
0400	5.7	85	0.28	6.0			17.2	1960			1540
0500	5.5	92	0.31	6.0			17.5	1960			
0600	2.0	83	0.3	3.4			21.0	1830			
0700	4.5	76	0.2	4.3			17.5	1840	"	"	"
0800	7.5	105	–	–			–	–	–	–	–
0900	5.6	102	–	–			18.2	1820	1560	1620	1540
1000	5.6	90	0.3	6.75			17.5	1820			
1100	6.0	89	0.31	6.5			17.5	1810			
1200	6.0	95	0.30	6.5			17	1800			
1300	6.5	97	0.29	6.5			16	1960			
1400	6.0	90	0.30	6.29			16	1960			
1500	5.5	82	0.30	6.1			16	1960			
1600	5.5	84	0.30	6.0			15	1960		"	
1700	6.0	84	0.30	6.0			15.5	1870		1630	
1840	7.0	83	0.3	6.0			13.5*	1960		1620	
1900	5.2	64	0.3	6.1	"		12.5*	1960	"	1620	"

* Probe moved upstream to be on other side of scrubber

– Note: ADL sampling performed from 1200 to 1500.

TABLE C-3

PROCESS DATA FOR COKE PLANT WASTE TEST
DATE 4.28.76
(STEADY STATE)

Waste Feed Rate	20.8 liter/hr	5.5 gal/hr
High Pressure Air Feed Rate	0.043 cu m/min	1.52 cfm
Catalyst Addition Rate	1.1 liter/hr	0.3 gal/hr
Reactor Residence Time	1.15 hr	1.15 hr
Reactor Temperature	279.2 °C	534.6 °F
Reactor Pressure	107 atm	1560 psig
Oxygen Concentration in Gas Vent*	16.3%	16.3%
Effluent Gas Vent Rate	2.51 cu m/hr	89.0 cfh
	0.042 cu m/min	1.5 cfm
Approximate Amount of Waste Fed During Total Run	606 liters	160 gal

*Inside Simpro trailer

TABLE C-4

PROCESS DATA FOR ARTHUR WASTE TEST
DATE 4.29.76

Time	Flow Rates: Waste Feed GPH	Fuel GPH	Catalyst Additions GPH	Liquid Effluent GPH	H.P. Air Additions: Reactor	Reactor 1	Excess O_2 %	Pressures, psig: H.P. Air PT-1	Waste Feed PT-2	Catalyst Feed PT-3	Reactor 1 Outlet PT-11
					Avg. 2.84 cu mfm (1.7 cfm)						
0500	5.6	102	0.3	5.9			6.2	1850	1560	1620	1570
0630	6.6	86	0.27	6.4			3.4	1850	1560	1620	
0730	6.8	77	0.27	6.2			3.6	1840		1620	
0830	4.0	81	0.32	6.6			7.5	1820		1620	
0900	5.5	95	0.28	6.2			8.5	1830		1650	
1000	-	105	0.28	6.2			9.0	1850		1690	
1100	6.5	105	0.36	6.25			8.5	1870		1820	
1200	6.5	107	0.30				9.2	1960		1790	
1300	6.8	95	0.29				10.5	1900		1800	
1400	6.5	98	0.29				7.0	1910		1910	
1500	6.5	76	0.29	6.1			1.5	1900		1950	
1600	4.5	81	-	-			2.0	1900		2150	

* Note: ASL sampling performed from 1030 to 1330.

TABLE C-5

PROCESS DATA FOR ARCHCAMP WASTE TEST
DATE 4-29-76

Temperatures °F

Time	Feed 1	OLI Preheater 2	R-1 Feed 3	R-1 Bottom 5	R-1 Top 6	R-2 Feed 7	R-2 Bottom 8	R-2 Top 9	Cooler Outlet 14	PCV Outlet 15	OLI Head Tank 19	OLI Mixer Motor 21	OLI Heater Element 24
0500	76	572	551	541	539	532	537	537	141	121	74	169	574
0600	77	573	556	539	540	533	543	543	138	120	74	167	579
0700	79	579	559	539	539	531	541	546	135	120	74	170	583
0800	80	574	555	535	539	532	542	542	137	119	76	173	583
0900	80	576	557	538	537	530	542	542	137	119	78	172	581
1000	81	571	551	535	535	530	541	541	133	115	79	171	578
1100	80	574	552	540	538	531	541	547	140	120	80	172	580
1200*	80	567	546	534	536	531	541	533	136	115	80	171	570
1300	80	567	547	529	531	525	538	538	135	116	79	170	571
1400	80	539	539	538	539	531	540	540	132	117	79	170	561
1500	80	540	537	539	541	537	548	548	131	117	79	171	546
1600	81	521	501	525	531	532	540	543	132	122	78	169	541

* Note: OLI sampling performed from 1030 to 1130.

TABLE L-6

PROCESS DATA FOR AMIBEN® WASTE TEST
DATE 4.29.76
(STEADY STATE)

Waste Feed Rate	24.2 liter/hr	6.4 gal/hr
High Pressure Air Feed Rate	0.048 cu m/min	1.7 cfm
Catalyst Addition Rate	1.1 liter/hr	0.3 gal/hr
Reactor Residence Time	~1 hr	~1 hr
Reactor Temperature	280.9 °C	537.7 °F
Reactor Pressure	107 atm	1580 psig
Excess Oxygen Concentration in Gas Vent*	6.8%	6.8%
Effluent Gas Vent Rate	3.86 cu m/hr	102 cfh
	0.048 cu m/min	1.7 cfm
Approximate Amount of Waste Fed During Total Run	303 liters	80 gal

*Analog Simpro trailer

APPENDIX D

ASSESSMENT OF ENVIRONMENTAL IMPACT OF DESTROYING CHEMICAL WASTES AT ZIMPRO, INC. SUBSIDIARY OF STERLING DRUG, INC. ROTHSCHILD, WISCONSIN 54474

The wet air oxidation process will be evaluated for its capability of destroying the following chemical wastes:

Coke Plant Wastes from the Iron and Steel Industry
Amines Wastes from General Aniline and Film

Initial consideration of the chemical characteristics of these wastes by ZIMPRO has resulted in the recommendation that the pilot plant mounted on the movable trailer be used because it has a titanium reactor vessel which will be more resistant to the corrosion characteristics of the wastes than the other pilot plant reactors. This pilot plant has a nominal capacity of 8.4 gallons per hour with a maximum air flow rate of 5 SCFM. The emissions to the environment will be the off-gases from a scrubber following the air/liquid separator and the liquid effluents from the reactor. It is not anticipated that any solid waste residues will result that would require special disposal since the shipping drums will be cleaned at the plant; however, it is possible that the treated wastes might contain some solids as a slurry either because these are present in the wastes as received or because oxidation changes solubility limits of dissolved substances.

The trailer mounted wet air oxidation pilot plant will be located within the pilot plant building at ZIMPRO's headquarters in Rothschild, Wisconsin. This facility is located in a semi-rural area which is surrounded by a considerable growth of trees indigenous to the area. The area has almost the appearance of a national park with deer and other wildlife present. The nearest neighbors are residential homes within about 500 yards. Other residences are located along a major roadway; however, the total population in the Town of Rothschild is less than 3,500. Other businesses are located in the general area the largest of which is a kraft paper mill estimated to be within 3 kilometers. This paper mill has the characteristic odor of reduced sulfur compounds which would be definitely noticeable in the ZIMPRO area when the prevailing winds are in the right direction. Although there is considerable vehicular traffic on I-51 (business), the ZIMPRO facilities are located at the end of a cul-de-sac; consequently, the only vehicular traffic will be employees' automobiles and the occasional delivery trucks. The indoor location of the pilot plant and the nature of the equipment (small sized pumps and compressors) should not cause a detectable noise level outside the area. The highly oxidative conditions maintained in the reactor should suppress the generation of particularly odorous substances and the scrubber off-gases emitted to the atmosphere through a roof vent should not create either an odor or visual problem. Although there is apt to be a visible steam plume due to the relatively low ambient air temperatures, it should be very small and will probably dissipate rapidly.

The greatest potential for adverse environmental impact is expected to be related to the water effluent. The potential for adverse impact from air emissions and disposal of shipping containers and any residues should be quite low. Before discussing the potential impact and the method to be employed to minimize the impact, it is well to recognize that the components identified in the wastes have widely varying degrees of toxicity. Information taken from the Registry of Toxic Effects of Chemical Substances - 1975 Edition lists the following pertinent information for identified substances.

Coke Plant Wastes*

Phenol	Oral - human - TDLo - 14 mg/kg
	Oral - human - LCLo - 140 mg/kg
	USOS - Air - TWA - 5 ppm (19 mg/m^3)
Aniline	Oral - human - LDLo - 350 mg/kg
	USOS - Air - TWA - 5 ppm (19 mg/m^3)
o-Cresol	Rat - LD50 - 121 mg/kg
	USOS - Air - TWA - 5 ppm (19 mg/m^3)
p-cresol	Rat - LD50 - 207 mg/kg
	USOS - Air - TWA - 5 ppm (19 mg/m^3)
Napthalene	Child - LDLo - 100 mg/kg
	USOS - Air - TWA - 10 ppm (38 mg/m^3)
Quinoline	Rat - oral - LD50 - 460 mg/kg
Indole	Rat - oral - LD50 - 1000 mg/kg
Dimethylphenols	Rat - LD50 varies from 444 to 3200 mg/kg
Ammonia	Inhalation - human LCLo - 10,000 ppm/5 hr
	Inhalation - human TCLo - 20 ppm
	USOS - Air - 50 ppm
Hydrocyanic Acid	Oral - human - LDLo - 570 mg/kg
	Inhalation - human - LCLo - 120 mg/m^3/1 hr
	USOS - Air - TWA - 10 ppm (38 mg/m^3)

Amiben Wastes*

Amiben	Rat - oral - LD50 - 3500 mg/kg

* Definition of Terms

TDLo	Lowest published toxic dose
LDLo	Lowest published lethal dose
USOS	U. S. Occupational Standard
TWA	Time weighted average
LD50	Lethal dose - 50 percent kill
TCLo	Lowest published toxic concentration
LCLo	Lowest published lethal concentration

Storage and Handling

The total quantity of wastes will be limited to six 55-gallon barrels. Upon receipt, these will be inspected for leakage by ZIMPRO research engineers assigned to the project and will be stored indoors on the concrete floor immediately adjacent to the test facility. Any leakage or spillage will be absorbed with a solid absorbent. The saturated absorbent would be placed into a State of Wisconsin approved landfill operated by ZIMPRO on their property.

Discussions with the waste suppliers indicate that personnel handling these wastes should take precautions to prevent skin contact; otherwise, no special precautions are necessary. By far the most hazardous component of any is the cyanide in the coke oven wastes; however, the cyanide exists undoubtedly in a highly complexed form in these alkaline wastes. Therefore, precautions should be taken to insure that the coke oven wastes are never made highly acidic and air stripped in an enclosed space since the cyanide can be readily removed as gaseous by hydrocyanic acid. ZIMPRO has recognized the potential problems with cyanides and has available equipment for emergency treatment of cyanide poisoning. There will be a characteristic odor, especially from the coke oven wastes, in the immediate vicinity; however, this odor should not be apparent beyond the property boundaries.

While it may be necessary to take precautions such as limiting exposure to drum contents, it is not believed that undue impacts are apt to occur in the immediate vicinity. The emptied drums will be washed and the wastewater treated or handled by the same procedures described in the ensuing discussions on water effluents. The cleaned drums will be stored and, subsequently, reused by ZIMPRO.

Water Effluents

Since wet air oxidation must be carried out in an aqueous medium for these wastes, the resulting wastewater stream must be carefully evaluated for further disposal. It is expected that the water effluents will contain chemical substances which will prohibit direct discharge into receiving waters, i.e., further treatments such as biochemical oxidation or activated carbon adsorption may be required. In order to achieve the required treatment, the water effluents will be collected during the run period and tested to determine if they can be degraded in the Rothschild wastewater treatment plant which is operated by ZIMPRO. While it is anticipated that the wastes will be degraded to a degree permitting their introduction into a biological wastewater treatment plant, if this does not occur additional treatment such as a more severe oxidation will be performed. The cognizant authority for permitting the Rothschild wastewater treatment plant is the Department of Natural Resources of the State of Wisconsin which is aware of the experimental nature of ZIMPRO's operations.

Air Emissions

It is believed that there is little potential for environmental impact occurring from the routine emission of the small volume of saturated air (estimated to be in the vicinity of 5 SCFH at 100-150°F) since it will have been scrubbed prior to release. The off-gases will contain carbon dioxide and nitrogen as the major components; however, some highly volatile substances might report to the gas stream although the physico-chemical relationships expected should limit these to nuisance levels, e.g., odors. Should these occur, the most immediate impact would probably be observed by ZIMPRO employees because of the low level at which the off-gases will be emitted. If a catastrophic failure of the high pressure process equipment occurred, there would probably be a large release of dissolved gases and flashing of water to steam; however, this will probably be of more concern from an occupational safety and health impact than an environmental impact.

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